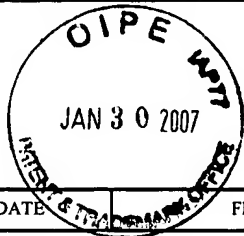




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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/522,928	01/24/2005	Ichiro Sato	TIP 031	6652

7590 01/23/2007
Gary C Cohn
4010 Lake Washington Boulevard Ne
Suite 105
Kirkland, WA 98033

EXAMINER

BUTTNER, DAVID J

ART UNIT	PAPER NUMBER
----------	--------------

1712

SHORTENED STATUTORY PERIOD OF RESPONSE	MAIL DATE	DELIVERY MODE
3 MONTHS	01/23/2007	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

If NO period for reply is specified above, the maximum statutory period will apply and will expire 6 MONTHS from the mailing date of this communication.

Office Action Summary	Application No. 10/522,928	Applicant(s) SATO, ICHIRO	
	Examiner David Buttner	Art Unit 1712	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

- 1) ☐ Responsive to communication(s) filed on ____.
- 2a) ☐ This action is **FINAL**. 2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

- 4) ☒ Claim(s) 1-10 is/are pending in the application.
 4a) Of the above claim(s) ____ is/are withdrawn from consideration.
- 5) ☐ Claim(s) ____ is/are allowed.
- 6) ☒ Claim(s) 1-3 is/are rejected.
- 7) ☒ Claim(s) 4-10 is/are objected to.
- 8) ☐ Claim(s) ____ are subject to restriction and/or election requirement.

Application Papers

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on ____ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.
 Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).
 Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

- 12) ☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
 a) ☒ All b) ☐ Some * c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
 2. ☐ Certified copies of the priority documents have been received in Application No. ____.
 3. ☒ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

- | | |
|--|--|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892) | 4) <input type="checkbox"/> Interview Summary (PTO-413)
Paper No(s)/Mail Date. ____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948) | 5) <input type="checkbox"/> Notice of Informal Patent Application |
| 3) <input checked="" type="checkbox"/> Information Disclosure Statement(s) (PTO/SB/08)
Paper No(s)/Mail Date <u>9/2/05;9/2/05</u> | 6) <input type="checkbox"/> Other: ____ |

Art Unit: 1712

The amendment of 1/24/05 was not entered as proper status identifiers are missing.

It is noted that the machine translation of JP2001200151 was provided by applicant without the translation of the critical final ~50 paragraphs.

Claims 4-10 objected to under 37 CFR 1.75(c) as being in improper form because a multiple dependent claim must refer to other claims in the alternative and cannot from other multiply dependent claims. See MPEP § 608.01(n). Accordingly, the claims 4-10 not been further treated on the merits.

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

Claims 1-3 rejected under 35 U.S.C. 103(a) as being unpatentable over Umeyama EP1188792 in view of JP2001200151.

Umeyama exemplifies (tables 3-11) blends of polycarbonate, branched polymethylphenylsiloxane, a sulfonate salt and PTFE. The polymethylphenylsiloxane has a high degree of branching and a high amount of phenyl groups (table 1). The blends may additionally include phosphorous flame retarders (paragraph 34). Phosphazene flame retarders are not named.

Phosphazene flame retarders are known to be effective in polycarbonates when used in combination with sulfonate salts or polymethylphenylsiloxanes (see table of

Art Unit: 1712

JP2001200151). The phosphazene would be also effective when used with both polysiloxane and organic salt (paragraph 83 of JP2001200151).

It would have been obvious to use a phosphazene flame retardant as the phosphorous flame retardant called for by Umeyama. AN improvement in flame retardancy would be expected.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to David Buttner whose telephone number is 571-272-1084. The examiner can normally be reached on weekdays from 10 to 5pm.

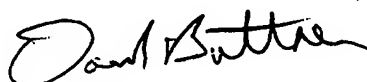
If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Randy Gulakowski, can be reached on 571-272-1302. The fax phone number for the organization where this application or proceeding is assigned is 571-273-8300.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

David Buttner

DAVID J. BUTTNER
PRIMARY EXAMINER

1/16/07





PTO/SB/08A (08-03)

Approved for use through 07/31/2008. OMB 0351-0031

U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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Institute for form 1449/PTO


**INFORMATION DISCLOSURE
STATEMENT BY APPLICANT**

(Use as many sheets as necessary)

Sheet **1** of **3****Complete if Known**

Application Number	10/522,928
Filing Date	24 January 2005
First Named Inventor	Sato
Art Unit	
Examiner Name	
Attorney Docket Number	TIP 031

U. S. PATENT DOCUMENTS					
Examiner Initials*	Cite No. ¹	Document Number	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
		Number-Kind Code ² (if known)			
DB ↓ ↓		US- 5,514,740	05-07-1996	Miyake et al.	
		US- 6,291,585	09-18-2001	Tomari et al.	
		US- 4,837,280	06-1989	Awaji	
		US- 5,236,633	08-17-1993	Satake et al.	
		US- 3,956,235	05-11-1976	Pasternack et al.	
		US- 5,354,514	10-11-1994	Satake et al.	
		US-			
		US-			
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		US-			
		US-			

FOREIGN PATENT DOCUMENTS						
Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear	T ⁶
		Country Code ³ Number ⁴ Kind Code ⁵ (if known)				
DB		EP 0 216 412	04-01-1987	Akzo N.V.		
		EP 0 351 875 (Eq. US 5,354,514)	01-24-1990	Jujo Paper Co.		
		JP 5 163400A	06-29-1993			✓
		JP 5-163405A	06-29-1993			✓
		JP 5-163426A	06-29-1993			✓
		JP 8-073653A	03-19-1996			✓

Examiner Signature	/David Buttner/	Date Considered	01/11/2007
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. ¹ Applicant's unique citation designation number (optional). ² See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. ³ Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). ⁴ For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁵ Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁶ Applicant is to place a check mark here if English language translation is attached.

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

If you need assistance in completing the form, call 1-800-PTO-9199 (1-800-786-9199) and select option 2.

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Substitute for form 1448/PTO

INFORMATION DISCLOSURE STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Complete if Known


Application Number	10/522,928
Filing Date	24 January 2005
First Named Inventor	Sato
Art Unit	
Examiner Name	
Attorney Docket Number	TIP 031

Sheet 2 of 3

U. S. PATENT DOCUMENTS

[illegible]

FOREIGN PATENT DOCUMENTS

Examiner Initials*	Cite No. ¹	Foreign Patent Document	Publication Date	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages Or Relevant Figures Appear	†
		Country Code ² Number ⁴ *Kind Code ³ (if known)	MM-DD-YYYY			
DB		JP 05-163408	06-29-1993	Daicel Chemical		✓
		JP 2001-226575	08-21-2001	Otsuka Chem.		✓
		JP 2001-200151	07-24-2001	Otsuka Chem.		✓

Examiner Signature	/David Buttner/	Date Considered	01/11/2007
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*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant. ¹Applicant's unique citation designation number (optional). ²See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. ³Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). ⁴For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. ⁵Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. ⁶Applicant is to place a check mark here if English language Translation is attached.

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INFORMATION DISCLOSURE
STATEMENT BY APPLICANT

(Use as many sheets as necessary)

Complete if Known

Application Number 10/552,928

Filing Date 24 January 2005

First Named Inventor Sato

Art Unit

Examiner Name

Sheet 3

of 3

Attorney Docket Number TIP 031

NON PATENT LITERATURE DOCUMENTS

Examiner Initials ²	Cite No. ¹	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc.), date, page(s), volume-issue number(s), publisher, city and/or country where published.	T ²
DB		CA Assession No. 127:222026, "Nontoxic marine antifouling coating with sustained effects", Taniguchi et al., 08-12-1997	
DB		CA Assession No. 131:318952, "Polymeric controlled-release microbicides", Ghosh, (1999)	

Examiner
Signature

/David Buttner/

Date
Considered

01/11/2007

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

1 Applicant's unique citation designation number (optional). 2 Applicant is to place a check mark here if English language Translation is attached.

This collection of information is required by 37 CFR 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 2 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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Notice of References Cited	Application/Control No. 10/522,928	Applicant(s)/Patent Under Reexamination SATO, ICHIRO	
	Examiner David Buttner	Art Unit 1712	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
	A	US-			
	B	US-			
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N	EP-1188792	03-2002	EP	Umeyama	----
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Machine translation of JP2001200151.
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

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L3 ANSWER 27 OF 38 CA COPYRIGHT 2007 ACS on STN
 AN 135:123337 CA
 ED Entered STN: 16 Aug 2001
 TI Transparent fire-resistant polycarbonate compositions and their moldings
 with good mechanical properties
 IN Tada; Yuji; Yabuhara, Tadao; Takase, Hiroyuki
 PA Ohtsuka Chemical Co., Ltd., Japan; Otsuka Chemical Holdings Co., Ltd.
 SO Jpn. Kokai Tokkyo Koho, 15 pp.
 CODEN: JKXXAF
 DT Patent
 LA Japanese
 IC ICM C08L069-00
 ICS C08J005-00; C08K005-5399; C08L069-00; C08L085-02; C08L083-04
 CC 37-6 (Plastics Manufacture and Processing)
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	JP 2001200151	A	20010724	JP 2000-6667	20000114
	JP 3605719	B2	20041222		
PRAI	JP 2000-6667		20000114		

CLASS

PATENT NO.	CLASS	PATENT FAMILY CLASSIFICATION CODES
JP 2001200151	ICM	C08L069-00
	ICS	C08J005-00; C08K005-5399; C08L069-00; C08L085-02; C08L083-04
	IPCI	C08L0069-00 [ICM,7]; C08J0005-00 [ICS,7]; C08K0005-5399 [ICS,7]; C08K0005-00 [ICS,7,C*]; C08L0069-00 [ICS,7]; C08L0085-02 [ICS,7]; C08L0085-00 [ICS,7,C*]; C08L0083-04 [ICS,7]; C08L0083-00 [ICS,7,C*]
	IPCR	C08J0005-00 [I,C*]; C08J0005-00 [I,A]; C08K0005-00 [I,C*]; C08K0005-5399 [I,A]; C08L0069-00 [I,C*]; C08L0069-00 [I,A]
AB		The compns. contain (a) 100 parts aromatic polycarbonates, (b) 0.1-40 parts ≥ 1 cyclic, linear, and/or crosslinked phenoxyphosphazene compds., and (c) 0.01-50 parts ≥ 1 compds. chosen from organic alkali metal salts, organic alkaline earth metal salts, and organopolysiloxanes. Thus, a composition containing Iupilon S 2000F (polycarbonate) 100, diphenoxyphosphazene oligomer (prepared from dichlorophosphazene oligomer and sodium phenolate) 2.5, and potassium perfluorobutanesulfonate 0.20 part was injection-molded to give a test piece showing UL-94 rating V-0, no burning drops, and haze 5.4%.
ST		transparent fireproofing arom polycarbonate molding; polyphenoxyphosphazene potassium perfluorobutanesulfonate organopolysiloxane fireproofing polycarbonate
IT		Polysiloxanes, uses RL: MOA (Modifier or additive use); USES (Uses) (TSF 4300; transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)
IT		Carboxylic acids, uses RL: MOA (Modifier or additive use); USES (Uses) (alkaline earth salts; transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)
IT		Sulfonates RL: MOA (Modifier or additive use); USES (Uses) (alkali metal or alkaline earth metal salts; transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)
IT		Carboxylic acids, uses RL: MOA (Modifier or additive use); USES (Uses) (alkali metal salts; transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)
IT		Alkaline earth salts

RL: MOA (Modifier or additive use); USES (Uses)
(carboxylates; transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT Phosphorus acids
RL: MOA (Modifier or additive use); USES (Uses)
(esters, alkali metal or alkaline earth metal salts; transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT Polyphosphazenes
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PRP (Properties); PREP (Preparation); USES (Uses)
(phenoxy; transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT Fire-resistant materials
Fireproofing agents
(transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT Alkali metal salts
Alkaline earth salts
RL: MOA (Modifier or additive use); USES (Uses)
(transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT Polycarbonates, properties
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT Molded plastics, properties
RL: PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT 26085-02-9DP, Polydichlorophosphazene, reaction products with sodium phenolate
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PRP (Properties); PREP (Preparation); USES (Uses)
(oligomer; transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT 80-05-7DP, Bisphenol A, reaction products with dichlorophosphazene polymer, phenol, and sodium phenolate 80-09-1DP, Bisphenol S, reaction products with dichlorophosphazene polymer, phenol, and sodium phenolate 108-95-2DP, Phenol, reaction products with dichlorophosphazene polymer, hydroquinone, and sodium phenolate, preparation 123-31-9DP, Hydroquinone, reaction products with dichlorophosphazene polymer, phenol, and sodium phenolate 139-02-6DP, Sodium phenolate, reaction products with dichlorophosphazene oligomer 28212-48-8P, Polydiphenoxyphosphazene
RL: IMF (Industrial manufacture); MOA (Modifier or additive use); PRP (Properties); PREP (Preparation); USES (Uses)
(transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT 29420-49-3, Potassium perfluorobutanesulfonate
RL: MOA (Modifier or additive use); USES (Uses)
(transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

IT 24936-68-3, Lupilon S 2000F, properties 25037-45-0
RL: POF (Polymer in formulation); PRP (Properties); TEM (Technical or engineered material use); USES (Uses)
(transparent fire-resistant polycarbonate compns. for moldings with good mech. properties)

Disclaimer:

This English translation is produced by machine translation and may contain errors. The JPO, the INPIT, and those who drafted this document in the original language are not responsible for the result of the translation.

Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

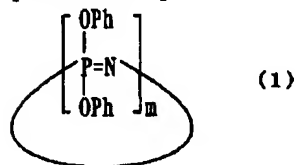
Translated: 06:26:18 JST 01/17/2007

Dictionary: Last updated 12/22/2006 / Priority: 1. Chemistry

CLAIMS**[Claim(s)]**

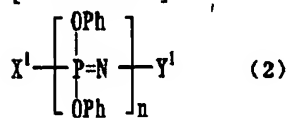
[Claim 1] In an aromatic-polycarbonate-resin 100 weight part, (A) (B) annular phenoxy phosphazene compound, At least one sort of phenoxy phosphazene compounds 0.1 - 40 weight parts, and (C) organicity alkali metal salt which were chosen from the chain-like phenoxy phosphazene compound and the bridge formation phenoxy phosphazene compound, The fire-resistant polycarbonate resin composition characterized by the thing which is chosen from organic alkaline earth metal salt and organopolysiloxane, and which blended at least one sort of 0.01 - 50 weight parts.

[Claim 2] (B) The annular phenoxy phosphazene compound of a component is a general formula (1).

[Formula 1]

In the inside m of [type, the integer of 3-25 is shown. Ph shows a phenyl group. The fire-resistant polycarbonate resin composition according to claim 1 which is annular phenoxy phosphazene expressed with].

[Claim 3] (B) The chain-like phenoxy phosphazene compound of a component is a general formula (2).

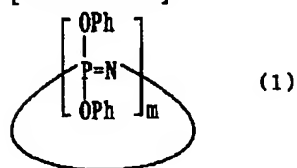
[Formula 2]

In the inside X^I of [type, group-N=P (OPh)₃ or group-N=P(O) OPh is shown, and Y^I is a

group. - P(OPh) 4 or group-P(O) (OPh)₂ are shown. n shows the integer of 3-10000. Ph is the same as the above. The fire-resistant polycarbonate resin composition according to claim 1 which is chain-like phenoxy phosphazene expressed with]

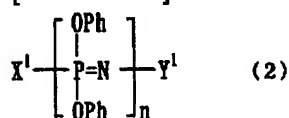
[Claim 4] (B) The bridge formation phenoxy phosphazene compound of a component is a general formula (1).

[Formula 3]



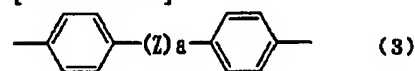
In the inside m of [type, the integer of 3-25 is shown. Ph shows a phenyl group. The annular phenoxy phosphazene and the general formula (2) which are expressed with]

[Formula 4]



In the inside X1 of [type, group-N=P (OPh)₃ or group-N=P(O) OPh is shown, and Y1 is a group. - P(OPh) 4 or group-P(O) (OPh)₂ are shown. n shows the integer of 3-10000. Ph is the same as the above. At least one sort of phosphazene compounds chosen from the group which consists of chain-like phenoxy phosphazene expressed with] are o-phenylene group, m-phenylene group, p-phenylene group, and a general formula (3).

[Formula 5]



In the inside Z of [type, -C(CH₃)₂-, -SO₂-, -S-, or -O- is shown. a shows 0 or 1. It is the compound over which it comes to construct a bridge by at least one sort of bridge formation machines chosen from the group which consists of a screw phenylene group expressed with]. (a) This bridge formation machine intervenes between two oxygen atoms from which the phenyl group of the phosphazene compound was desorbed. (b) The content ratio of a phenyl group is 50 to 99.9% on the basis of the total of the above-mentioned phosphazene compound (1) and/or all the phenyl groups in (2). And the fire-resistant polycarbonate resin composition according to claim 1 which is a bridge formation phenoxy phosphazene compound which does not have a free hydroxyl group in (c) intramolecular.

[Claim 5] The organic alkali metal salt and the organic alkaline earth metal salt of a component (C) The alkali metal salt of organic sulfonic acid, The alkali metal salt of organophosphate, the alkali metal salt of organic carboxylic acid, The fire-resistant polycarbonate resin composition

according to claim 1 which is at least one sort chosen from the alkaline earth metal salt of organic sulfonic acid, the alkaline earth metal salt of organophosphate, and the alkaline earth metal salt of organic carboxylic acid.

[Claim 6] (C) The fire-resistant polycarbonate resin composition according to claim 1 whose organopolysiloxane of a component is a phenyl content siloxane compound.

[Claim 7] Claim 1, Claim 2, Claim 3, Claim 4, the fire-resistant polycarbonate resin Plastic solid that can fabricate and obtain a fire-resistant polycarbonate resin composition according to claim 5 or 6.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a fire-resistant polycarbonate resin composition. Furthermore, this invention relates to the polycarbonate resin composition which has the advanced fire retardancy which does not show the dropping phenomenon at the time of combustion in detail, without aromatic polycarbonate resin spoiling the transparency and mechanical physical properties which it originally has.

[0002]

[Description of the Prior Art] Aromatic polycarbonate resin is excellent in mechanical hardness (especially impact property-proof), an electrical property, transparency, etc., and is broadly used in the field with various electricity and electric device fields, a car and the machine field, construction fields, etc. The field of which advanced fire retardancy is required focusing on OA equipment, and electricity and the electric device field is in these fields of the invention.

[0003] Although an oxygen index is high and aromatic polycarbonate resin is [oxygen index] resin which generally has self-extinguishing in various thermoplastics, in order that OA equipment, electricity and the electric device field, and a demand when [safe] it can set to a various application in addition to this may be filled, Furthermore, it is required that the feature of the transparency which raising fire retardancy and aromatic polycarbonate resin originally have should be held.

[0004] Various kinds of methods of blending organic halide, and organicity or inorganic sulfonate are conventionally known as the fire retardancy-ized method of aromatic polycarbonate resin.

[0005] Specifically, it is how (JP,S54-52152,A) to blend deca bromo diphenyloxide with aromatic polycarbonate resin, for example, How to blend with aromatic polycarbonate resin the aromatic polycarbonate of 2 and 2-bis(4-hydroxy 3, 5-dibromo phenyl) propane (= tetrabromobisphenol A) by which the end blockade was carried out by halogenation phenol (JP,S47-41422,B), The method (JP,S47-24660,B, JP,S47-44537,B, JP,S55-25466,A) of

adding the oligomer of tetrabromobisphenol A to aromatic polycarbonate resin is known. However, these methods have the fault which the thermal stability at the time of shaping falls since the halogenated compound is added, and generates corrosive or toxic gas and smoke at the time of shaping or combustion.

[0006] Moreover, generally, if organic halide is used together with antimony oxide compounds (for example, antimony trioxide, sodium antimonate, etc.), halogenation antimony is generated at the time of combustion, the surface is covered, continuation of combustion is checked, and raising fire retardancy is known. This technology is applied widely ("chemistry manual edited by applied chemistry the fifth edition" references, such as publication Maruzen Co., Ltd. edited by the Chemical Society of Japan, (1995), II, and the 423rd page). However, even when organic halide and an antimony oxide compound are used together, the fault which there is no change in having added the halogenated compound, and the thermal stability at the time of shaping falls like the above, and generates corrosive or toxic gas and smoke at the time of shaping or combustion arises.

[0007] Moreover, the method of blending the alkali metal salt of perfluoro alkane sulfonate with aromatic polycarbonate resin (JP,S47-40445,B, JP,S54-32456,B), How to blend the metal salt of aromatic series sulfonamide (JP,S56-45945,B), How to blend the metal salt of aliphatic series ether sulfonic acid (JP,S54-106562,B), the method (JP,S57-28424,B --) of blending the metal salt of aromatic series sulfonic acid The method (JP,S54-68857,A, JP,S55-27303,A) of blending JP,S58-43099,B, JP,S58-13587,B, and the sulfate metal salt of alcohols is indicated. However, by these methods, the aromatic-polycarbonate-resin (for example, about 1.5mm in thickness) mold goods which have the advanced fire retardancy which all does not show a dropping phenomenon at the time of combustion and which carried out thinning are not obtained. In order to acquire fire retardancy sufficient with these compounds, spoiling the transparency which is the characteristics which needed to carry out abundant addition and excelled [resin] in aromatic polycarbonate resin, and becoming opaque is not avoided.

[0008] Moreover, the thing for which an organic alkali metal salt and alkaline earth metal salt are mixed to aromatic polycarbonate, and polytetrafluoroethylene is added further, Although the method (JP,S60-38418,B) of preventing dropping at the time of combustion is indicated, in this technology, there is a fault that the transparency which is the original feature of aromatic polycarbonate is spoiled.

[0009] Furthermore, organophosphate is also the compound (JP,H7-41653,A) known from the former as a flame retarder. Although transparency is held even if it carries out abundant addition at aromatic polycarbonate resin, in order for this organophosphate to satisfy fire retardancy, there is a tendency to add organophosphate so much and for resin to be plasticized at a sake, heat deflection temperature becomes low, and mechanical properties, such as shock resistance, get worse. On the other hand, in order to take out fire retardancy

effectively by addition of a little organophosphate, the method of adding the poly fluoroalkane, for example, polytetrafluoroethylene, further for the purpose of the dropping prevention at the time of combustion is known (JP,S59-36657,B, JP,H6-45747,B). However, it is inescapable that the transparency of aromatic polycarbonate is lost by addition of polytetrafluoroethylene by this method.

[0010] On the other hand, in order to improve the fire retardancy of aromatic polycarbonate resin, the method of carrying out copolymerization of the polysiloxane to aromatic polycarbonate or the method of adding silicone resin is known. For example, in order to obtain fire-resistant polycarbonate resin the method (JP,S63-289059,A --) of using the mixture of an aromatic polycarbonate organopolysiloxane copolymer or an aromatic polycarbonate organopolysiloxane copolymer, and aromatic polycarbonate resin JP,H1-210462,A and JP,H4-202465,A are known. However, the polycarbonate resin whose aromatic polycarbonate organopolysiloxane copolymer independent fire-resistant performance is still inadequate and which was excellent in fire retardancy is not yet obtained.

[0011] Moreover, in order to obtain a flame-retardant-resin constituent the method (JP,S62-60421,B --) of blending various silicone resin with aromatic polycarbonate resin JP,S63-31513,B, a JP,3-48947,B number, JP,H6-128434,A, JP,H7-78171,B, JP,H7-33971,A, JP,H10-139964,A, and JP,H11-140294,A are indicated. However, the compound which has the above-mentioned siloxane copolymer or siloxane structure like silicone resin has a small fire retardancy-ized effect, and unless it adds so much, an effective fire-resistant effect cannot be demonstrated. if the amount of addition is increased in order to acquire sufficient fire retardancy -- many physical properties, such as the moldability of a resin composition thing, and appearance of mold goods, mechanical hardness, -- large -- not falling -- since it does not obtain and silicone resin is used so much, it is not avoided that the resin composition thing itself becomes expensive. Moreover, the dispersibility and compatibility of silicone resin to aromatic polycarbonate resin are not enough, two components from which a refractive index differs in moldings carry out phase separation, and there is also a problem that do not become low [transparency] or only a thing opaque when there are many loadings is obtained.

[0012] Therefore, the physical characteristic of aromatic polycarbonate resin and optical transparency are maintained, and development of the technology which gives usable inexpensive and advanced fire retardancy to the use of the large range is desired.

[0013]

[Problem(s) to be Solved by the Invention] This invention makes it a technical problem to offer the polycarbonate resin composition which has the advanced fire retardancy which does not show the dropping phenomenon at the time of combustion, without aromatic polycarbonate resin spoiling the transparency and the mechanical property which it originally has.

[0014]

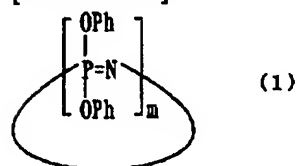
[Means for Solving the Problem] In order that this invention person may solve the above-mentioned technical problem, as a result of repeating research wholeheartedly, [a (A) aromatic-polycarbonate-resin 100 weight part] (B) At least one sort of phenoxy phosphazene compounds 0.1 - 40 weight parts, and (C) organicity alkali metal salt which were chosen from the annular phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound, and the bridge formation phenoxy phosphazene compound, The resin composition thing which is chosen from organic alkaline earth metal salt and organopolysiloxane and which blends at least one sort of 0.01 - 50 weight parts found out that it could become a desired fire-resistant polycarbonate resin composition. This invention is completed based on this knowledge.

[0015] Namely, this invention [a 1.(A) aromatic-polycarbonate-resin 100 weight part] (B) At least one sort of phenoxy phosphazene compounds 0.1 - 40 weight parts, and (C) organicity alkali metal salt which were chosen from the annular phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound, and the bridge formation phenoxy phosphazene compound, The fire-resistant polycarbonate resin composition which is chosen from organic alkaline earth metal salt and organopolysiloxane and which blends at least one sort of 0.01 - 50 weight parts.

2.(B) The annular phenoxy phosphazene compound of a component is a general formula (1).

[0016]

[Formula 6]

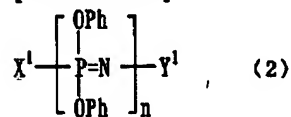


[0017] In the inside m of [type, the integer of 3-25 is shown. Ph shows a phenyl group. The fire-resistant polycarbonate resin composition of one above-mentioned description which is annular phenoxy phosphazene expressed with].

3.(B) The chain-like phenoxy phosphazene compound of a component is a general formula (2).

[0018]

[Formula 7]



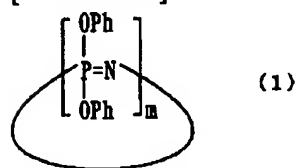
[0019] In the inside X1 of [type, group-N=P (OPh)₃ or group-N=P(O) OPh is shown, and Y1 is a group. - P(OPh)₄ or group-P(O) (OPh)₂ are shown. n shows the integer of 3-10000. Ph is the same as the above. The fire-resistant polycarbonate resin composition of one above-

mentioned description which is chain-like phenoxy phosphazene expressed with].

4.(B) The bridge formation phenoxy phosphazene compound of a component is a general formula (1).

[0020]

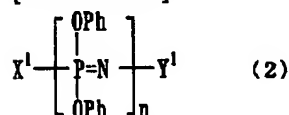
[Formula 8]



[0021] In the inside m of [type, the integer of 3-25 is shown. Ph shows a phenyl group. The annular phenoxy phosphazene and the general formula (2) which are expressed with]

[0022]

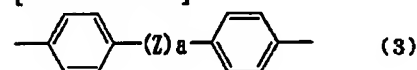
[Formula 9]



[0023] In the inside X1 of [type, group-N=P (OPh)3 or group-N=P(O) OPh is shown, and Y1 is a group. - P(OPh) 4 or group-P(O) (OPh)2 are shown. n shows the integer of 3-10000. Ph is the same as the above. At least one sort of phosphazene compounds chosen from the group which consists of chain-like phenoxy phosphazene expressed with] are o-phenylene group, m-phenylene group, p-phenylene group, and a general formula (3).

[0024]

[Formula 10]



[0025] In the inside Z of [type, -C(CH3)2-, -SO2-, -S-, or -O- is shown. a shows 0 or 1. It is the compound over which it comes to construct a bridge by at least one sort of bridge formation machines chosen from the group which consists of a screw phenylene group expressed with].

(a) This bridge formation machine intervenes between two oxygen atoms from which the phenyl group of the phosphazene compound was desorbed. (b) The content ratio of a phenyl group is 50 to 99.9% on the basis of the total of the above-mentioned phosphazene compound (1) and/or all the phenyl groups in (2). And a fire-resistant polycarbonate resin composition given in the above 1 which is the bridge formation phenoxy phosphazene compound which does not have a free hydroxyl group in (c) intramolecular.

The organic alkali metal salt and the organic alkaline earth metal salt of a component 5.(C) Alkali metal salt of organic sulfonic acid, The alkali metal salt of organophosphate, the alkali

metal salt of organic carboxylic acid, The fire-resistant polycarbonate resin composition of one above-mentioned description which is at least one sort chosen from the alkaline earth metal salt of organic sulfonic acid, the alkaline earth metal salt of organophosphate, and the alkaline earth metal salt of organic carboxylic acid.

6.(C) Fire-resistant polycarbonate resin composition of one above-mentioned description whose organopolysiloxane of component is phenyl content siloxane compound.

7. Fire-resistant polycarbonate resin Plastic solid which can fabricate and obtain fire-resistant polycarbonate resin composition of description to the above 1, 2, 3, 4, 5, or 6.

[0026] The polycarbonate resin composition which has the advanced fire retardancy which does not show the dropping phenomenon at the time of combustion is offered without aromatic polycarbonate resin spoiling the transparency and the mechanical properties (for example, shock resistance, dimensional stability, thermal stability, etc.) which it originally has according to this invention.

[0027]

[Embodiment of the Invention] (A) as aromatic polycarbonate resin of the (A) component used for component this invention It is the thermoplastic aromatic polycarbonate polymer or copolymer which is obtained by making carbonyl halide or carbonic acid diester react in an aromatic dihydroxy compound, or this and a little polyhydroxy compounds and which may branch.

[0028] As an aromatic dihydroxy compound, a well-known thing can be used widely conventionally. When the typical example of an aromatic dihydroxy compound is given, 2 and 2-bis(4-hydroxyphenyl) propane (= bisphenol A), 2 and 2-bis(3, 5-dibromo 4-hydroxyphenyl) propane (= tetrabromobisphenol A), Bis(4-hydroxyphenyl) methane, 1, and 1-bis(4-hydroxyphenyl) ethane, 2 and 2-bis(4-hydroxyphenyl) butane, 2, and 2-bis(4-hydroxyphenyl) octane, 2 and 2-bis(4-hydroxy 3-methylphenyl) propane, 1, and 1-bis(3-t-butyl 4-hydroxyphenyl) propane, 2 and 2-bis(4-hydroxy 3, 5-dimethylphenyl) propane, 2 and 2-bis(3-bromo 4-hydroxyphenyl) propane, 2, and 2-bis(3, 5-dichloro 4-hydroxyphenyl) propane, 2 and 2-bis(3-phenyl 4-hydroxyphenyl) propane, 2, and 2-bis(3-cyclohexyl 4-hydroxyphenyl) propane, 1, and 1-screw (4-hydroxyphenyl 1-phenyl ethane) The bis(hydroxy aryl) alkane illustrated by bis(4-hydroxyphenyl) diphenylmethane etc.; 1 and 1-bis(4-hydroxyphenyl) cyclopentane, The bis(hydroxy aryl) cycloalkanes illustrated by 1 and 1-bis(4-hydroxyphenyl) cyclohexane etc.; 4 and 4'-dihydroxy diphenyl ether, 4 and 4'-dihydroxy 3, dihydroxy diaryl ether; 4 illustrated with - dimethyl diphenyl ether etc., 3'4'-dihydroxydiphenyl sulfide, 4 and 4'-dihydroxy 3, dihydroxy diaryl sulfide; 4 illustrated by - dimethyl diphenyl sulfide etc., 3'4'-dihydroxydiphenyl sulfoxide, 4 and 4'-dihydroxy 3, dihydroxy diaryl sulfoxide; 4 illustrated by - dimethyl diphenyl sulfoxide etc., 3'4'-dihydroxy diphenylsulfone, 4 and 4'-dihydroxy 3, 3'dihydroxy diaryl sulfone; hydroquinone [which is illustrated by - dimethyl diphenylsulfone

etc.], resorcinol, 4, 4'-dihydroxydiphenyl, etc. are mentioned.

[0029] In this invention, these aromatic dihydroxy compounds are independent, or two or more sorts may use them, mixing. In these aromatic dihydroxy compounds, bis(4-hydroxyphenyl) alkane system especially 2, and 2-bis(4-hydroxyphenyl) propane is used suitably.

[0030] Moreover, in this invention, to the above-mentioned aromatic dihydroxy compound, a polyhydroxy compound can be used together as a branching-ized agent in the 0.01-3mol% of range, and can also be made into branching-ized polycarbonate. As a polyhydroxy compound, can use a well-known thing widely conventionally, and For example, FURORO glycine, 2, the 6-dimethyl 2, 4, 6-bird (4-hydroxyphenyl)-3-heptene, 4, the 6-dimethyl 2, 4, 6-bird (4-hydroxyphenyl)-2-heptene, 1, 3, 5-bird (2-hydroxyphenyl) benzole, 1, 1, and 1-bird (4-hydroxyphenyl) ethane, 2, 6-bis(2-hydroxy 5-methylbenzyl)-4-methyl phenol, alpha, alpha', the polyhydroxy compound illustrated with alpha"-bird (4-hydroxyphenyl)-1, 3, and 5-triisopropyl benzene etc., etc. are mentioned.

[0031] Moreover, as carbonyl halide or carbonic acid diester, a well-known thing can be used widely conventionally, and dialkyl carbonate, such as diaryl carbonate and dimethyl carbonate, such as carbonyl chloride and diphenyl carbonate, and diethyl carbonate, etc. is specifically mentioned.

[0032] Generally the viscosity average molecular weight converted from the methylene chloride solution viscosity at 25 degrees C of aromatic polycarbonate resin is 15,000-60,000 preferably on 10,000-100,000, shaping, or the physical properties of mold goods.

[0033] In this invention, it faces manufacturing the aromatic polycarbonate resin which has such viscosity average molecular weight, and the catalyst for promoting a suitable molecular weight modifier and a suitable reaction etc. can also be added if needed. for example, as a } monovalent aromatic hydroxy compound suitable for adjusting molecular weight Specifically Phenol, m-methyl phenol, p-methyl phenol, Halogenation objects, such as alkylation objects, such as m-propyl phenol, p-propyl phenol, p-tert-butylphenol, p-tert-octyl phenol, p-cumyl phenol, and p-long chain alkylation phenol, and p-bromine phenol, etc. are mentioned.

[0034] Aromatic polycarbonate resin of the (A) component used by this invention may be independent one sort, and what was mixed two or more sorts is sufficient as it.

(B) The phenoxy phosphazene compound of the (B) component used as a flame retarder in component this invention is at least one sort chosen from the annular phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound, and the bridge formation phenoxy phosphazene compound. As such a phenoxy phosphazene compound, a well-known thing can be used widely conventionally.

[0035] As an annular phenoxy phosphazene compound, the annular phenoxy phosphazene compound expressed with the above-mentioned general formula (1), for example can be mentioned.

[0036] As a chain-like phenoxy phosphazene compound, the chain-like phenoxy phosphazene compound expressed with the above-mentioned general formula (2), for example can be mentioned.

[0037] As a bridge formation phenoxy phosphazene compound [for example, at least one sort of phosphazene compounds chosen from the group which consists of chain-like phenoxy phosphazene expressed with the annular phenoxy phosphazene and the general formula (2) which are expressed with the above-mentioned general formula (1)] It is the compound over which it comes to construct a bridge by at least one sort of bridge formation machines chosen from the group which consists of a screw phenylene group expressed with o-phenylene group, m-phenylene group, p-phenylene group, and the above-mentioned general formula (3). (a) This bridge formation machine intervenes between two oxygen atoms from which the phenyl group of the phosphazene compound was desorbed. (b) The content ratio of a phenyl group can mention the bridge formation phenoxy phosphazene compound which does not have the hydroxyl group free to (c) intramolecular which is 50 to 99.9% on the basis of the total of the above-mentioned phosphazene compound (1) and/or all the phenyl groups in (2).

[0038] (B) Also in the phenoxy phosphazene compound of a component, a bridge formation phenoxy phosphazene compound is suitable.

[0039] ["not having a free hydroxyl group in a molecule"] in this invention When a fixed quantity is carried out according to the acetylating method by acetic anhydride and pyridine of a description with an analytical chemistry manual (the 3rd edition of revision, the edited by Japan Society for Analytical Chemistry, Maruzen Co., Ltd., 1981) of page [353rd], it means that the free amount of hydroxyl groups is below a limit of detection. A limit of detection is a limit of detection as a hydroxyl equivalent per 1g of samples (bridge formation phenoxy phosphazene compound of this invention), and are more specifically below 1×10^{-6} hydroxyl equivalent / g here.

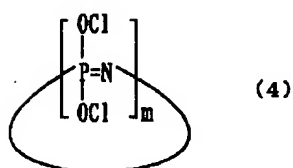
[0040] In addition, [if the bridge formation phenoxy phosphazene compound of this invention is analyzed by the above-mentioned acetylation method, the quantity of the hydroxyl group of the raw material phenol which remains will also be added, but] Since raw material phenol is made in fixed quantity with high performance chromatography, only a fixed quantity of free hydroxyl groups in a bridge formation phenoxy phosphazene compound can be carried out.

[0041] The annular phenoxy phosphazene compound and chain-like phenoxy phosphazene compound which are used by this invention are a known compound.

[0042] The bridge formation phenoxy phosphazene compound of this invention is also a well-known compound, for example, it is a general formula (4).

[0043]

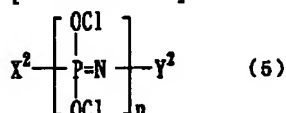
[Formula 11]



[0044] It is the same as the above the inside m of [type. Annular dichlorophosphazene and the general formula (5) which are expressed with]

[0045]

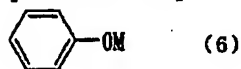
[Formula 12]



[0046] In the inside X2 of [type, group-N=PCl3 or group-N=P(O) Cl is shown, and Y2 is a group. - PCl4 or group-P(O) Cl2 is shown. n is the same as the above. To at least one sort of dichlorophosphazene compounds chosen from the group which consists of normal chain-like dichlorophosphazene expressed with], it is a general formula (6).

[0047]

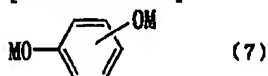
[Formula 13]



[0048] In the inside M of [type, an alkali metal is shown. The alkali metal phenolate expressed with], and a general formula (7)

[0049]

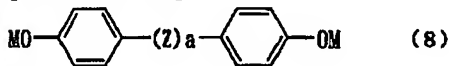
[Formula 14]



[0050] It is the same as the above the inside M of [type. Alkali metal JIFENORATO and the general formula (8) which are expressed with]

[0051]

[Formula 15]



[0052] It is the same as the above the inside Z, a, and M of [type. It is manufactured by what you make a mixture with at least one sort of JIFENORATO chosen from the group which consists of alkali metal JIFENORATO expressed with] react (the first process), and is made for the above-mentioned alkali metal phenolate to react to the compound subsequently obtained further (the second process).

[0053] [the dichlorophosphazene compound expressed with the general formula (4) and general formula (5) which are used as one of the raw materials in the above-mentioned manufacturing method] For example, JP,S57-87427,A, JP,S58-19604,B, JP,S61-1363,B, JP,S62-20124,B, H, R, Allcock work, "Phosphorus-Nitrogen Compounds", Academic Press, (1972), J.E. Mark, H.R.Allcock, R.West work, "Inorganic Polymers"Prentice-Hall According to the well-known method of a description, it can manufacture to International, Inc. (1992), etc.

[0054] If the example is shown, first in chlorobenzene or tetrachloroethane [ammonium chloride and phosphorus pentachloride (or ammonium chloride, phosphorus trichloride, and chlorine) / making it react at about 120-130 degrees C and carrying out demineralization oxidation] The dichlorophosphazene compound expressed with the general formula (5) the dichlorophosphazene compound expressed with the general formula (4) whose m is 3-25, and whose n are 3-25 can be manufactured. These dichlorophosphazene compounds (dichlorophosphazene oligomer) are usually obtained as a mixture.

[0055] moreover, it was obtained by having done in this way -- [mixture / of annular and the shape of a chain / dichlorophosphazene oligomer / with distillation or recrystallization] Annular dichlorophosphazene compounds, such as hexachlorocyclotriphosphazene, octachlorocyclotetraphosphazene, and deca KURORU cyclopentaphosphazene, The dichlorophosphazene compound by which n is expressed with the general formula (5) which is 25-10000 can be manufactured by heating and carrying out ring opening polymerization of the hexachlorocyclotriphosphazene to 220-250 degrees C.

[0056] With dichlorophosphazene of annular and the shape of a chain mixed, it may dissociate and the dichlorophosphazene compound manufactured above may be used independently respectively.

[0057] As alkali metal phenolate expressed with a general formula (6), a well-known thing can be used widely conventionally, for example, sodium phenolate, potassium phenolate, lithium phenolate, etc. can be mentioned. These alkali metal phenolate can use one sort independently, or can use two or more sorts together.

[0058] In alkali metal JIFENORATO expressed with a general formula (7), they are two groups. - OM (M is the same as the above) may be in alt.** meta or which physical relationship of Para. As an example of this alkali metal JIFENORATO, alkali metal salts, such as resorcinol, hydroquinone, and catechol, can be mentioned, for example. Also in these, sodium salt and lithium salt are desirable. This alkali metal JIFENORATO can use one sort independently, or can use two or more sorts together.

[0059] As alkali metal JIFENORATO expressed with a general formula (8) For example, alkali metal salts, such as 4 and 4'-isopropylidene diphenol (bisphenol A), 4, and 4 '- sulfonyl diphenol (bisphenol S), 4, 4'-thiodiphenol, 4, and 4 '- oxy-diphenol, 4, 4'-diphenol, etc. can be mentioned. Also in these, sodium salt and lithium salt are desirable. This alkali metal

JIFENORATO can use one sort independently, or can use two or more sorts together.

[0060] In this invention, alkali metal JIFENORATO expressed with alkali metal JIFENORATO and the general formula (8) which are expressed with a general formula (7) may be used independently, respectively, and these may be mixed and used.

[0061] In the first process of the manufacturing method of this invention so that the chlorine atom in a dichlorophosphazene compound may not be altogether consumed by a reaction with alkali metal phenolate and alkali metal JIFENORATO That is, it is desirable to adjust the amount of alkali metal phenolate and the alkali metal JIFENORATO used as the chlorine atom in a dichlorophosphazene compound remains in addition also by a reaction with alkali metal phenolate and alkali metal JIFENORATO. Thereby, both-OM group (M is the same as the above) of alkali metal JIFENORATO combines with the phosphorus atom of a dichlorophosphazene compound. At the first process, the amount of alkali metal phenolate and the alkali metal JIFENORATO used should just usually make about 0.05-0.9Eq preferably about 0.1-0.8Eq by the total quantity of both phenolate on the basis of the chlorinity of a dichlorophosphazene compound.

[0062] In the second process of the manufacturing method of this invention, it is desirable to adjust the amount of the alkali metal phenolate used so that all of all of the chlorine atom and the free hydroxyl group in the compound generated at the first process of the above may be consumed by a reaction with alkali metal phenolate. In this invention, the amount of the alkali metal phenolate used should just usually make about 1-1.5Eq preferably about 1-1.2Eq on the basis of the chlorinity of a dichlorophosphazene compound.

[0063] this invention -- the use rate (alkali metal JIFENORATO / alkali metal phenolate --) of alkali metal phenolate (total quantity used at the first process and the second process), and alkali metal JIFENORATO A molar ratio should just usually be preferably set to 1 / 20 - 1/6 2000 to about [per /] 1/4.

[0064] the reaction of the first process and the second process -- each usual room temperature - it is preferably carried out under the temperature of about 80-140 degrees C, and about 150 degrees C is usually completed preferably in about 3 to 7 hours for about 1 to 12 hours. Each reaction of the first process and the second process is usually performed in organic solvents, such as halogenated-aromatics hydrocarbons, such as aromatic hydrocarbon, such as benzene, toluene, and xylene, mono-chlorobenzene, and dichlorobenzene.

[0065] The bridge formation phenoxy phosphazene compound of this invention manufactured by the above-mentioned reaction follows the usual isolation methods, such as washing, filtration, and desiccation, from a reaction mixture, easily, can isolate and can be refined, for example.

[0066] The bridge formation phenoxy phosphazene compound of this invention is in within the limits whose decomposition temperature is 250-350 degrees C.

[0067] [moreover, the content ratio of the phenyl group in the bridge formation phenoxy phosphazene compound of this invention] It is 50 to 99.9% on the basis of the total of all the phenyl groups in the annular phenoxy phosphazene of a general formula (1), and/or the normal chain-like phenoxy phosphazene of a general formula (2), and is 70 to 90% preferably.

[0068] in addition, when the end groups X1 and Y1 in a general formula (2) change with reaction conditions etc., and are the usual reaction conditions and a mild reaction is performed, for example by the system of non-water X1 becomes $-N=P(OPh)_3$ and Y1 becomes the structure of $-P(OPh)_4$. When it reacts on severe reaction conditions which are reaction conditions to which moisture or alkali metal hydroxide exists in the system of reaction, or a transition reaction produces X1 will be in the state where X1 other than the structure of $-P(OPh)_4$ is intermingled by $-N=P(OPh)_3$ and Y1, and the thing of the structure of $-P(O)(OPh)_2$ is intermingled by $-N=P(O)OPh$ and Y1.

[0069] The loadings of the phenoxy phosphazene compound which is the (B) component in this invention need to be within the limits of 0.1 - 40 weight part to the component 100 weight part (above-mentioned [A]). (B) When there are few loadings of the phenoxy phosphazene compound which is a component than 0.1 weight part, a fire-resistant effect is not demonstrated, but when 40 weight parts are exceeded conversely, cause the machine physical-properties fall of the aromatic-polycarbonate-resin Plastic solid acquired. As for the loadings of the phenoxy phosphazene compound which is the (B) component in this invention, it is desirable to consider it as the range of 0.3 - 20 weight part to the component 100 weight part (above-mentioned [A]).

[0070] In this invention, [the ring of the (B) component, the shape of a chain, and a bridge formation phenoxy phosphazene compound] When decomposing or burning, harmful gas or smoke to a living thing, such as hydrogen halide, are not generated, and the corrosion of a metal pattern, deterioration of resin, and coloring are not started from not containing halogen, such as chlorine and bromine, at the time of resin shaping. Moreover, the phenoxy phosphazene compound of this invention does not reduce the molding temperature of resin, and its volatility is low and it does not have blocking or that ooze out (JUSHINGU) and problems, such as dripping at the time of combustion, arise at the time of kneading.

[0071] [moreover, the bridge formation phenoxy phosphazene compound of this invention] Since it is the bridge formation phenoxy phosphazene compound which does not have the one end hydroxy group of a dihydroxy compound substantially, the molecular weight of aromatic polycarbonate resin is not reduced and the characteristics of resin original, such as mechanical properties, such as shock resistance, a heat-resisting property, shaping workability, and transparency, are not reduced.

(C) In component this invention, at least one sort chosen from an organic alkali metal salt, organic alkaline earth metal salt, and organopolysiloxane is used as a (C) component.

[0072] Although various kinds of things are known as an organic alkali metal salt or organic alkaline earth metal salt, in this invention, at least one sort chosen from the organic acid or the alkali metal salt of organic acid ester which has at least one carbon atom, or alkaline earth metal salt is used.

[0073] Here, it may be organic sulfonic acid, organic carboxylic acid, organophosphate, etc., and halogen like fluorine, chlorine, and bromine may be replaced and ester of an organic acid or an organic acid may be oligomer or polymer further. As oligomer and polymer, polymer, oligomer, etc. which have a sulfonyl group, a carboxyl group, a phospho group, etc. can be mentioned, for example to the intramolecular of polymer, such as polystyrene, or oligomer.

[0074] As organic sulfonic acid, for example 1-propane sulfonic acid, 1-hexane sulfonic acid, And aliphatic series sulfonic acid, such as 3-(2-methoxyethoxy)-1-propane sulfonic acid, 1 and 1-difluoro 1-butane sulfonic acid, 1, 1, and 2-trifluoro 4-methoxy 1-butane sulfonic acid, 1, 1, 2, 3, 3, and 3-hexafluoro 1-propane sulfonic acid, Perfluoro methansulfonic acid, perfluoro ethane sulfonic acid, perfluoro propane sulfonic acid, perfluoro butane sulfonic acid, perfluoro methyl butane sulfonic acid, perfluoro hexane sulfonic acid, perfluoro heptane sulfonic acid, And fluorine-containing alkane sulfonic acid, such as a perfluorooctane sulfonate, Benzenesulfonic acid, p-iodobenzene sulfonic acid, naphthalene 2, 6-disulfon acid, Naphthalene Trisul Hong acid, 2, 5-dichloro benzenesulfonic acid, 3, 4-dichloro benzenesulfonic acid, 2, 4, and 5-trichlorobenzene sulfonic acid, 4, and 4'-dibromo diphenyl 3-sulfonic acid, 2, 3, 4, 5, 6-PENTA chloro beta-styrene sulfonic acid, 4 and 4'-dichloro diphenyl sulfide 3-sulfonic acid, a tetra-chlorodiphenyl ether disulfon acid, - dichloro benzophenone 3, a 4 and 4'3'-disulfon acid, 2, 5-dichloro thiophene 3-sulfonic acid, Diphenylsulfone 3-sulfonic acid, diphenylsulfone 3, a 3'-disulfon acid, 2, 4, 6-bird chloro 5-sulfoisophtharate dimethyl, 2, 4, 5-trichlorobenzene sulfonic acid dichlorophenyl, And aromatic series sulfonic acid, such as 4'-[1, 4, 5, 6, 7, 7'-hexa chloro bicyclo [2, 2, 1]-hept 5-****-, and -****] benzenesulfonic acid, etc. is mentioned.

[0075] As organic carboxylic acid, for example Hexane carboxylic acid, heptane carboxylic acid, octane carboxylic acid, Perfluoro methane carboxylic acid, perfluoro ethane carboxylic acid, perfluoro propane carboxylic acid, perfluoro butane carboxylic acid, perfluoro methyl butane carboxylic acid, perfluoro hexane carboxylic acid, perfluoro heptane carboxylic acid, Perfluoro octane carboxylic acid etc. is mentioned.

[0076] As organophosphate, JI (p-t-buthylphenyl) phosphoric ester, JI (p-cumyl phenyl) phosphoric ester, JI (bromination phenyl) phosphoric ester, etc. are mentioned, for example.

[0077] On the other hand, sodium, potassium, lithium, caesium, etc. are mentioned as an alkali metal, and magnesium, calcium, strontium, barium, etc. are mentioned as an alkaline earth metal.

[0078] (C) as the organic alkali metal salt and the organic alkaline earth metal salt of a component Specifically The alkali metal salt of organic sulfonic acid, the alkali metal salt of

organophosphate, The alkali metal salt of organic carboxylic acid, the alkaline earth metal salt of organic sulfonic acid, It is the alkaline earth metal salt of organophosphate, and the alkaline earth metal salt of organic carboxylic acid, and the salt of sodium, such as organic sulfonic acid, organophosphate, and organic carboxylic acid, potassium, and caesium is especially suitable.

[0079] In the resin composition thing of this invention, the organic alkali metal salt and alkaline earth metal salt of the (C) component may be used by an one-sort independent, and may be used combining two or more sorts. Moreover, the loadings of the organic alkali metal salt which is the (C) component, or alkaline earth metal salt are 0.01 - 50 weight part to a (A) resin 100 weight part. If this quantity exceeds 50 weight parts, while the physical properties of aromatic polycarbonate resin are spoiled, it will become disadvantageous economically. On the contrary, if it becomes less than 0.01 weight part, the fire retardancy of a resin composition thing or a Plastic solid will fall.

[0080] In this invention, the desirable loadings of the organic alkali metal salt which is the (C) component, or alkaline earth metal salt are the range of 0.05 - 20 weight part from the field of resin physical properties and economical efficiency to a (A) component 100 weight part.

[0081] As organopolysiloxane of the (C) component used by this invention, a phenyl content siloxane compound etc. is mentioned, for example. In a phenyl content siloxane compound, for example Pori (diphenyl) siloxane, Others [siloxane compounds /, such as Pori (methylphenyl) siloxane (= methylphenyl silicon), / phenyl content], A phenyl content siloxane polycarbonate copolymer, for example, a Pori (diphenyl) siloxane polycarbonate copolymer, A Pori (methylphenyl) siloxane polycarbonate copolymer, the copolymer which has the polycarbonate block guided from phenyl content siloxane and an aromatic polycarbonate block, etc. are included. These copolymers are more specifically indicated to JP,S63-289059,A, JP,H1-210462,A, JP,H4-202465,A, etc., and a thing can be widely used for them.

[0082] (C) Organopolysiloxane of a component is usually good 0.01 - 50 weight part and to carry out 0.05-20 weight part combination preferably to a (A) component 100 weight part. If there are more loadings of organopolysiloxane than 50 weight parts, the transparency of aromatic polycarbonate resin will be lost and the physical properties of this resin will also be spoiled. On the contrary, if it becomes less than 0.01 weight part, the fire retardancy of a resin composition thing or a Plastic solid will fall.

[0083] In this invention, as a (C) component, an organic alkali metal salt and organic alkaline earth metal salt may be used independently, and organopolysiloxane may be used independently, or these may be used together. The well-known additive usually used for fire-retardancy-izing in addition to the above (A), (B), and the (C) component can also be used for the resin composition thing of other component this inventions in the range which does not check the original transparency of aromatic polycarbonate resin, combining it suitably.

[0084] [the additive for fire-retardancy-izing] if the transparency of aromatic polycarbonate resin is usually held There is no restriction in particular, can use a well-known thing widely conventionally, and For example, the zinc oxide of the shape of a detailed grain, Metal oxides, such as tin oxide, iron oxide, molybdenum oxide, copper oxide, and manganese dioxide; Aluminium hydroxide, Metal hydroxides, such as magnesium hydroxide processed with magnesium hydroxide, zirconium hydroxide, the aluminium hydroxide that carried out oxalic acid treatment, and a nickel compound; Sodium carbonate, Antimony compounds, such as calcium carbonate, barium carbonate, antimony trioxide, antimony tetroxide, antimony pentoxide, and sodium antimonate, etc. can be mentioned. Moreover, chlorinated paraffin, par chloro cyclo pentadecane, tetrabromobisphenol A, Tetrabromobisphenol A epoxy oligomer or polymer, Screw (tribromo phenoxy) Organic salt matter or bromine compounds, such as ethane and bis(tetra-bromine FUTARU imino) ethane; Trimethyl phosphate, Triethyl phosphate, tributyl phosphate, trioctylphosphate, Tributoxyethyl phosphate, diisopropylphenyl phosphate, Octyl diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, Trixylyl phosphate, cresyl diphenyl phosphate, KISHIRIRU diphenyl phosphate, Phosphoric ester, such as bird RUJIKI silyl phosphate and (2-ethylhexyl) diphenyl phosphate; Hydroxyl group content phosphoric ester, Resorcinol screw (diphenyl) Phosphate and hydroquinone screw (diphenyl) Phosphate, Bisphenol A screw (diphenyl) Phosphate, resorcinol screw (JIKISHIRIRU) Phosphate, hydroquinone screw (JIKISHIRIRU) Phosphate, Condensed-phosphoric-acid ester compounds, such as bisphenol A bis(JITORIRU) phosphate, biphenol bis(JIKISHIRIRU) phosphate, and bisphenol A bis(JIKISHIRIRU) phosphate; Red phosphorus, A halogen content phosphoric ester compound, a halogen content condensed-phosphoric-acid ester compound, Phosphine oxide compounds, such as a phosphonate compound, triphenylphosphine oxide, and tritoyl phosphine oxide; Melamine, Melamine SHIANURETO, melamine phosphate, MERAMU, MEREMU, a melon, SAKUSHINO guanamine, guanidine sulfamate, ammonium sulfate, Nitrogen containing compounds, such as ammonium phosphate, polyphosphoric acid ammonium, and alkylamine phosphate; graphite, such as silicon compounds, such as boron compounds, such as zinc borate, metaboric acid barium, and ammonium borate, and silica, and thermal expansion nature, etc. can be used.

[0085] These additives may be used by an one-sort independent, and two or more sorts may be combined and they may be used.

[0086] Moreover, it can add in the resin composition thing of this invention, combining suitably a kind and the various resin additives of quantity, a filler, other synthetic resins, elastomers that do not check the character of this resin composition thing if needed further. As various resin additives, an ultraviolet ray absorbent, light stabilizer, an antioxidant, a protection-from-light agent, metal deactivator, a quencher, a heat-resistant stabilizer, a lubricant, a release agent, a colorant, an antistatic agent, an age resistor, a plasticizer, an impact strength improvement

agent, a compatibilizer, etc. are mentioned, for example.

[0087] In various resin additives, as an ultraviolet ray absorbent For example, a benzotriazol system, a benzophenone system, a SARISHI rate system, The ultraviolet ray absorbent of the oligomer which has an oxalic acid anilide system, a diphenyl cyanoacrylate system, triazine systems, and these frames, and a polymer system, and the ultraviolet ray absorbent of the inorganic system which consists of an ultrafine particle can be mentioned.

[0088] for example, as a benzotriazol system ultraviolet ray absorbent 2-[2'-hydroxy5'-(hydroxymethyl) phenyl]-2H-benzotriazol, 2-[2'-hydroxy5'-(hydroxyethyl) phenyl]-2H-benzotriazol, 2-[2'-hydroxy 3'-methyl 5'-(hydroxyethyl) phenyl]-2H-benzotriazol, 2-[2'-hydroxy 3'-t-butyl 5'-(hydroxyethyl) phenyl]-2H-benzotriazol, 2-[2'-hydroxy 3'-t-butyl 5'-(hydroxyethyl) phenyl]-5-chloro 2H-benzotriazol, A 2 and 2'-methylene screw [6-(5-chloro 2H-benzotriazol 2-IRU)-4-(2-hydroxyethyl) phenol], 2 and 2'-methylene screw [6-(2H-benzotriazol 2-IRU)-4-(3-hydroxypropyl) phenol], 2, 2'-methylene screw [6-(5-chloro 2H-benzotriazol 2-IRU)-4-(3-hydroxypropyl) phenol], A 2 and 2'-methylene screw [6-(2H-benzotriazol 2-IRU)-4-(2-hydroxypropyl) phenol], A 2 and 2'-methylene screw [6-(5-chloro 2H-benzotriazol 2-IRU)-4-(2-hydroxypropyl) phenol], A 2 and 2'-methylene screw [6-(5-chloro 2H-benzotriazol 2-IRU)-4-(4-hydroxy butyl) phenol], 6-(2H-benzotriazol 2-IRU)-4-(2-hydroxyethyl) phenol] ether, 2, and 2' bis[-] [6-(2H-benzotriazol 2-IRU)-4-(2-hydroxyethyl) phenol] sulfone etc. is mentioned.

[0089] As a triazine system ultraviolet ray absorbent, for example 2-(2, 4-dihydroxy phenyl)-4, 6-diphenyl s-triazine, 2-(2, 4-dihydroxy phenyl)-4, 6-bis(2, 4-dimethylphenyl)-s-triazine, 2-(2, 4-dihydroxy phenyl)-4, 6-bis(2, 4-dimethoxy phenyl)-s-triazine, 2-(2-hydroxy 4-(2-hydroxyethyl) phenyl)-4, 6-bis(2-hydroxy 4-dimethylphenyl)-s-triazine, 2-(2-hydroxy 4-(2-hydroxyethyloxy) phenyl)-4, 6-bis(2-hydroxy 4-dimethylphenyl)-s-triazine, 2-(2-hydroxy 4-(3-hydroxy propyloxy) phenyl)-4 and 6-bis(2-hydroxy 4-dimethylphenyl)-s-triazine etc. is mentioned.

[0090] As an antioxidant, a phenolic antioxidant, a sulfur system antioxidant, a phosphorus system antioxidant, etc. can be mentioned, for example.

[0091] As a phenolic antioxidant, for example 2, 6-G tert-butyl 4-methyl phenol, Pentaerythrityl tetrakis [3 -(3' and 5'-G tert-butyl 4'-hydroxyphenyl)- propionate], Octadecyl 3 -(3' and 5'-G tert-butyl 4'-hydroxyphenyl)- Propionate, A 2 and 2'-methylene screw (4-methyl 6-tert-butylphenol), A 2 and 2'-methylene screw (4-ethyl 6-tert-butylphenol), 4 and 4'-butylidenebis (3-methyl 6-tert-butylphenol), A 4 and 4'-thio screw (3-methyl 6-tert-butylphenol), 2 and 4-****- (normal octylthio)-6-4"-hydroxy 3', 5'-G tert-butylanilino-1, 3, 5-triazine, 2 and 2-****- diethylene screw [3 -(3' and 5'-G tert-butyl 4'-hydroxyphenyl)- propionate], N, and N'-hexamethylene screw (3, 5-G tert-butyl 4-hydroxy hydronalium thinner MAMIDO), 3 and 9-{2-[3-(3-butyl 4-hydroxy 5-methylphenyl) propionyloxy]-1 and 1-dimethyl ethyl}-tetraoxaspiro [2, 4, 8, and 10-] [5, 5] undecane etc. can be mentioned.

[0092] As a sulfur system antioxidant, for example Dilauryl-3,3'-thiodipropionate, *****- 3,

3'-thiodipropionate, dimyristyl 3, 3'-thiodipropionate, Distearyl 3, 3'-thiodipropionate, pentaerythrityl tetrakis (3-mercaptopropionate), pentaerythrityl tetrakis (3-laurylthio propionate) and screw {2-methyl 4-{3-normal alkyl (C12 --) Or C14 thio propionyloxy}-5-tert-buthylphenyl} sulfide, 2-mercapto vent imidazole, glycerol 3-stearyl thiopropionate, etc. can be mentioned.

[0093] As a phosphorus system antioxidant, for example Tris (nonyl phenyl) phosphite, Triphenyl phosphite, tris (2, 4-G tert-buthylphenyl) phosphite, Diphenyl isodecyl phosphite, diphenyl isooctylphosphite, Distearylpentaerythritoldiphosphite, JI (2, 4-G tert-buthylphenyl) pentaerythritoldiphosphite, tetrakis (2, 4-G tert-buthylphenyl)-4, and 4-BIFENIREJIHOSUHO night etc. can be mentioned.

[0094] As light stabilizer, for example 2-(2-hydroxy 5-tert-octyl phenyl) benzotriazol, 2-(3-tert-butyl 5-methyl 2-hydroxyphenyl)-5-chlorobenzo triazole, 2-(5-methyl 2-hydroxyphenyl) benzotriazol, 2-[2-hydroxy 3 and 5-bis(alpha and alpha-dimethylbenzyl) phenyl]-2H-benzotriazol, A 2 and 2'-methylene screw (4-cumyl 6-benzotriazol phenyl), 2, and 2'-p-phenylene screw (3, 1-benzoxazine 4-ON), polyalkylene naphthalate, etc. are mentioned.

[0095] As a filler, for example Mica, kaolin, a talc, silica, Clay, Calcium carbonate, calcium sulfate, calcium silicate, a glass bead, A glass balloon, a glass flake, glass fiber, alumina, titanium oxide, A fibrous titanic acid alkali metal, fibrous boric acid transition metal salt, fibrous boric acid alkaline earth metal salt, A zinc oxide whisker, a titanium oxide whisker, a magnesium oxide whisker, A gypsum-fibrous whisker, an aluminum silicate whisker, a calcium silicate whisker, A silicon carbide whisker, a titanium carbide whisker, a silicon nitride whisker, a titanium nitride whisker, carbon fiber, an alumina fiber, an alumina silica fiber, a zirconia fiber, quartz fiber, a metal fiber, etc. are mentioned.

[0096] Various above-mentioned additives and an above-mentioned filler may be used independently, or two or more sorts may use them, mixing.

[0097] As other synthetic resins and elastomers, when it mixes with polycarbonate resin, it can be used in the range which does not check the transparency, mixing suitably. For example, the polyester which consists of aromatic dicarboxylic acid or its derivative, and dihydric phenol or its derivative is mentioned.

[0098] It is possible to combine the compound which can secure fire retardancy or transparency as other additives further in this invention. For example, when resin burns, oxygenated oligomer which promotes carbonization of the resin or polymer, for example, polyethylene glycol, and a BORIBI nil alcohol are mentioned. Moreover, the oligomer or the polymer which makes a basic skeleton oxygenated compounds and these ether derivatives, such as trimethylolethane, TORIMECHI roll butane, propane trithiol, and pentaerythritol, an ester derivative, or said oxygenated compound is desirable. These may be used by an one-sort independent, may be combined two or more sorts and may be used.

[0099] The resin composition thing of this invention can be prepared by blending and kneading

each aforementioned component (A), (B) and the (C) component, and the various addition ingredients used if needed. The method usually used for combination and kneading, for example, a ribbon blender, It can carry out by the method of using a Henschel mixer, V type blender, a NAUTA mixer, a Banbury mixer, a drum tumbler, a single axis screw extruder, a twin screw extruder, a ko kneader, a multiaxial screw extruder, etc. In addition, the cooking temperature for kneading can usually be suitably chosen in 240-300 degrees C.

[0100] [the fire-resistant polycarbonate resin composition obtained thus] Shaping processing is easily possible by methods, such as the known various shaping methods, for example, extrusion, injection molding, compression molding, calender shaping, and rotational casting. Moreover, it can apply to blow molding, vacuum forming, gas injection shaping, etc., and can be conveniently used as a material of housings, such as an electron and an electric product with which the outstanding fire retardancy is demanded, and OA equipment, or a chassis use, and various parts.

[0101] Thus, the obtained resin composition thing can be used for the industrial fields, such as the electricity as which transparency is required, an electron, communication, agriculture-and-forestry fishery, mining, construction, food, fiber, clothing, Medical Science Division, coal, petroleum, rubber, leather, a car, precision instruments, wood, furniture, printing, and a musical instrument. For example, a printer, a personal computer, a word processor, a keyboard, PDA (small information terminal), Telephone, a facsimile, a copying machine, ECR (electronic formula cash register), a calculator, Office work and OA equipment, such as an electronic notebook, an electronic dictionary, curd, a holder, and stationery, A washing machine, a refrigerator, a cleaner, a microwave oven, a light, a game machine, an iron, Electrical household appliances and electrical equipment, such as a kotatsu, TV and VTR, a video camera, a digital camera, It is used for the use of electricity and electronic parts, such as AV equipment, such as a radio cassette recorder, a tape recorder, a mini disc, CD player, PD, DVD, a speaker, and a liquid crystal display, a connector, a switch, a cable, and a clock, communication equipment, etc. Moreover, a seat, belts (stuffing, the outer material, etc.), ceiling tension, the compartible top, An armrest, a door trim, a rear package tray, a carpet, a mat, A sun visor, a foil cover, a mattress cover, the air back, an insulating material, hanging -- a hand -- hanging -- ****, electric wire clothing material, electric insulation material, a coating material, and a coating material -- Upper tension material, a flooring material, ****, a deck panel, covers, a plywood, a ceiling board, a diaphragm, A side wall, a carpet, wallpaper, a wall covering material, exterior cases, interior material, roof material, a sound isolation board, Cars, such as an insulating board and a window material, vehicles, a vessel, an airplane and structural material, and clothing, The use of a life and sport leisure goods, such as a curtain, a sheet, a plywood, a synthetic fiber board, a carpet, a door mat, a sheet, a bucket, a hose, a container, glasses, a bag, a case, goggles, a ski outfit, a racket, a tent, a musical instrument,

and a toy, is mentioned.

[0102]

[Example] Although an example and a comparative example are hung up and this invention is clarified further hereafter, this invention is not limited to these. In addition, evaluation of the resin composition thing was performed by the following method.

[0103] Fire retardancy: Polycarbonate resin which carried out predrying 110 degrees C beforehand for 10 hours ((A) component), (B) A component, the (C) component, and other components were requirements-added, it mixed, the twin screw extruder (S1-KRC 25mm Kneader: Made by Kurimoto) was used, and it kneaded and pelletized with the cylinder temperature of 270 degrees C, and the nozzle temperature of 260 degrees C.

[0104] Obtained PERETSUTO 110 degrees C -- after 10-hour desiccation and injection molding machine (MINIMAT-26/15B --) Using the Sumitomo Heavy Industries, Ltd. make, [the cylinder temperature of 280 degrees C, and the tool temperature of 70 degrees C] A Plastic solid 1/16 inch (about 1.6mm) in thickness, 12.5mm in width, and 127mm in length is fabricated. The method of examining UL-94V (Test for) Flammability of Plastic Materials for Parts in Devices and Appliances Fire-resistant evaluation was performed according to UL 94 and Fourth Edition.

[0105] Average burning time: The number of flaming sum total seconds after every 2 times a total of 10 times of **** showed said fire-resistant examination to one-set five specimens.

[0106] Drip: In said fire-resistant examination, it ****(ed) a total of 10 times to five specimens, and the number of times of the flaming grain (drip) which ignites the cotton under 30cm was measured at the time of a combustion test.

[0107] HAZE: It is a specimen 3mm in thickness, 50mm in width, and 90mm in length like the case of the above and fire-resistant evaluation. It fabricates and is JIS. It applies to K-7105-1981 correspondingly, and is HAZE. METER (trade name: HAZE METER NDH 2000, Nippon Denshoku Industries, Inc. make) It used, HAZE (%) was measured and it was considered as the index of transparency.

[0108] synthetic example 1 phenoxy phosphazene (the mixture of $[N=P(-OPh)_2]_3$ and $[N=P(-OPh)_2]_4$ --) it abbreviates to "FR-1" hereafter. Synthetic H.R.Allcock work and "Phosphorus-Nitrogen Compounds -- " -- Academic following Press, (1972), and the method indicated to 151 -- FR-1 It manufactured.

[0109] Namely, after adding the toluene solution of sodium phenolate in 580g of 20% chlorobenzene solutions containing a dichlorophosphazene oligomer (62% of trimer, mixture of 38% of tetramer) 1.0 unit mole (115.9g) under churning, it reacted to them at 110 degrees C for 10 hours. The residual chlorinity of a product is <0.01% and checked that they were the following compounds.

[0110] $[N=P(-OPh)_2]_3$, example 2 of 4 synthesis Phenoxy phosphazene compound which has

the structure of cross linkage by Para Feni Wren (-- it abbreviates to "FR-2" hereafter.) -- phenol of 1.1mol (103.5g) of synthesis -- The toluene solution of sodium phenolate was prepared by carrying out heating flowing back of 1.1mol (44.0g) sodium hydroxide, 50g of water, and the toluene 500ml mixture, and removing only water besides a system.

[0111] In parallel to said reaction, in a 2l. 4 mouth flask, 0.15mol (16.5g) hydroquinone, 1.0mol (94.1g) phenol, 1.3mol (31.1g) lithium hydroxide, 52g of water, and a toluene 600ml mixture are put in, heating flowing back is carried out, and only water is removed besides a system. The toluene solution of the lithium salt of hydroquinone and phenol was prepared. It is a dichlorophosphazene oligomer (72% of trimer) to this toluene solution. After 580g of 20% chlorobenzene solutions as for which 15% of a tetramer, a pentamer and 8% of a hexamer, 3% of the amount object of seven, and more than an octamer contain 2% of mixture 1.0 unit mole (115.9g) were dropped below 30 degrees C under churning, the churning reaction of them was carried out at 110 degrees C for 4 hours. Next, after adding under churning the toluene solution of sodium phenolate prepared previously, the reaction was continued at 110 degrees C for 8 hours.

[0112] After it washed the reaction mixture 3 times in 1l. of sodium hydroxide aqueous solutions 3% after the end of a reaction, next 1l. of water washed 3 times, the organic layer was condensed under the reduced pressure. Concentration hardening by drying of the obtained product was carried out at 80 degrees C and 266Pa or less, and 211g white powder was obtained.

[0113] Hydrolysis chlorine of the bridge formation phenoxy phosphazene compound obtained above was 0.01% or less, and the presentation of the last thing was $[N=P(-O-p-Ph-O-) 0.15 (-O-Ph) 1.7]$ from phosphorus content and a CHN ultimate-analysis value.

[0114] The weight average molecular weight (Mw) was 1100 in polystyrene conversion (based on GPC analysis), TG/DTA analysis did not show the clear fusing point, but 306 degrees C and the 5% weight loss temperature of decomposition starting temperature were 311 degrees C.

[0115] Moreover, as a result of performing the fixed quantity of a residual hydroxy group by the acetylating method, it was below a limit of detection (considering it as the hydroxy equivalent per sample 1g : $1 \times 10^{-6} \text{Eq/(g)}$ or less).

Synthetic example 3 Phenoxy phosphazene compound which has the structure of cross linkage by a 2 and 2-bis(p-oxy-phenyl) isopropylidene machine (-- it abbreviates to "FR-3" hereafter.) -- 0.7mol (65.9g) of synthetic phenol and toluene 500ml was put into the 1l. 4 mouth flask, and under churning, keeping internal solution temperature at 25 degrees C, 0.65 gram atom (14.9g) metallic sodium was cut out finely, and was invested. Churning was continued for 8 hours until metallic sodium disappeared completely at 77-113 degrees C after the end of an injection.

[0116] It is parallel with said reaction and bisphenol A. 0.25mol (57.1g), 1.1mol (103.5g) of phenol and tetra-HIDORU furan (THF) 800ml was put into the 3l. 4 mouth flask, and under churning, keeping internal solution temperature at 25 degrees C, 1.6 gram atom (11.1g) metal lithium was cut out finely, and was thrown in. Churning was continued for 8 hours after the end of an injection until metal lithium disappeared completely at 61-68 degrees C. It is a dichlorophosphazene oligomer (72% of trimer) to this slurry solution. Under churning of 386g of 30% chlorobenzene solutions as for which 15% of a tetramer, a pentamer and 8% of a hexamer, 3% of the amount object of seven, and more than an octamer contain 2% of mixture 1.0 unit mole (115.9g), after being dropped over 1 hour, keeping internal solution temperature at 20 degrees C or less, it reacted at 80 degrees C for 4 hours. Subsequently, under churning, after adding the sodium phenolate solution prepared separately over 1 hour, keeping internal solution temperature at 20 degrees C, it reacted at 80 degrees C for 10 hours.

[0117] After the end of a reaction, the reaction mixture was condensed and 1l. of toluene was newly added except for THF. It is 2%NaOH about this toluene solution. After it washed 3 times at 1l., next 1l. of water washed 3 times, the organic layer was condensed under the reduced pressure. Concentration hardening by drying of the obtained product was carried out at 80 degrees C and 266Pa or less, and 230g white powder was obtained.

[0118] Hydrolysis chlorine of the bridge formation phenoxy phosphazene compound obtained above was 0.01% or less, and the presentation of the last thing was $[N=P(-O-Ph-C(CH_3)_2-Ph-O-)]_{0.25}(-O-Ph)_{1.50}$ from phosphorus content and a CHN ultimate-analysis value.

[0119] The weight average molecular weight (Mw) was 1140 in polystyrene conversion (based on GPC analysis), TG/DTA analysis did not show the clear fusing point, but 310 degrees C and the 5% weight loss temperature of decomposition starting temperature were 315 degrees C.

[0120] Moreover, as a result of performing the fixed quantity of residual hydroxyl by the acetylating method, it was below a limit of detection (considering it as the hydronalium KISHIRU equivalent per sample 1g : $1 \times 10^{-6} \text{Eq/(g)}$ or less).

Synthetic example 4 Phenoxy phosphazene which has the structure of cross linkage by 4 and 4-sulfonyl diphenylene (bisphenol S residue) (-- it abbreviates to "FR-4" hereafter.) -- [putting 0.4mol (37.6g) of synthetic phenol, and tetrahydrofuran (THF) 500ml into a 1l. 4 mouth flask, and keeping internal solution temperature at 25 degrees C under churning] 0.45 gram atom (9.2g) metallic sodium was cut out finely, and was invested. Churning was continued for 5 hours until metallic sodium disappeared completely at 65-72 degrees C after the end of an injection.

[0121] It is parallel with said reaction and they are 1.70mol (160.0g) of phenol, and Bisphenol S with a 1l. 4 mouth flask. 0.05mol (12.5g) is dissolved in THF500ml. 1.8 gram atom (41.4g) metallic sodium is invested below 25 degrees C, and it applies after the end of an injection for

1 hour, and is 61 degrees C. Churning was continued at **** and 61 degrees C - 68 degrees C for 6 hours, and the sodium phenolate mixed solution was prepared. This solution Dichlorophosphazene oligomer ([72% of a trimer, 15% of a tetramer, a pentamer, and 8% of hexamer]) The churning reaction was carried out at 71-73 degrees C after dropping under cooling / churning of 25 degrees C or less for 5 hours at 580g of 20% chlorobenzene solutions as for which 3% of the amount object of seven and more than an octamer contain 2% of mixture 1.0 unit mole (115.9g). Next, after the sodium phenolate mixed solution prepared previously was dropped, the reaction was continued at 71-73 degrees C for 10 hours.

[0122] After condensing the reaction mixture after the end of a reaction and remelting to chlorobenzene 500ml, sulfuric acid treatment, 5% sodium bicarbonate water washing, and three flushes were performed 3 times and 5%, concentration hardening by drying of the 5% NaOH water washing was carried out at 266Pa or less, and 220g of white solids were obtained.

[0123] Hydrolysis chlorine of the bridge formation phenoxy phosphazene compound obtained above is 0.01% or less, and the presentation of this thing was mostly determined as $[N=P(-O-Ph-SO_2-Ph-O-)]_{0.05}(-O-Ph)_{1.90}$ from phosphorus content and a CHN ultimate-analysis value.

[0124] The weight average molecular weight (Mw) was 1070 in polystyrene conversion, and, as for the melting temperature (Tm) by TG/DTA analysis, 334 degrees C and the 5% weight loss temperature of 103 degrees C and decomposition starting temperature were 341 degrees C.

[0125] Moreover, as a result of performing the fixed quantity of a residual hydroxy group by the acetylating method, it was below a limit of detection (considering it as the hydroxy equivalent per sample 1g : $1 \times 10^{-6} \text{Eq/(g)}$ or less).

[0126] Example 1 polycarbonate resin (trade name: you pyrone, S-2000F) Viscosity average molecular weight : 22,900, 100 weight parts by Mitsubishi Engineering, A FR-12.5 weight part and perfluoro butane sulfonic acid potassium (It abbreviates to "C-1" hereafter) After carrying out the dry blend of the 0.2 weight part beforehand, this invention resin composition thing of the pellet type was obtained by supplying and carrying out fusion extrusion of the cylinder temperature to the hopper of the biaxial extruder set as 270 degrees C (made by WAKO PURE CHEMICAL INDUSTRIES LTD.).

[0127] this invention resin composition thing was obtained like the example 1, respectively except having changed FR-1 in two to example 4 example 1 into FR-2, FR-3, or FR-4.

[0128] Except having changed C-1 in five to example 8 example 1 into methylphenyl silicon (trade name: TSF-4300, Toshiba Silicone, Inc. make) (it abbreviating to "C-2" hereafter), it blended as shown in Table 1, and this invention resin composition thing was obtained like the example 1, respectively.

[0129] this invention resin composition thing was obtained like the example 1, respectively except having added trimethylolethane (the WAKO PURE CHEMICAL INDUSTRIES LTD. make and the following abbreviating to "D-1") to the combination in nine to example 10 example 1, and an example 5.

[0130] The resin composition thing was obtained like the example 1, respectively except having changed as a comparative example 1 - 3 each compounding agent were shown in Table 1.

[0131] The loadings (loadings to a (A) component 100 weight part (weight part)) of the (B) component in the above-mentioned example 1-10 and a comparative example 1-3, the (C) component, and other components are shown in Table 1, and those evaluation results are shown in Table 2, respectively.

[0132]

[Table 1]

		(B)成分				(C)成分		D-1
		FR-1	FR-2	FR-3	FR-4	C-1	C-2	
実施例	1	2.50	—	—	—	0.20	—	—
	2	—	2.50	—	—	0.20	—	—
	3	—	—	2.50	—	0.20	—	—
	4	—	—	—	2.50	0.20	—	—
	5	2.50	—	—	—	—	0.30	—
	6	—	2.50	—	—	—	0.30	—
	7	—	—	2.50	—	—	0.30	—
	8	—	—	—	2.50	—	0.30	—
	9	2.50	—	—	—	0.20	—	1.00
	10	2.50	—	—	—	—	0.30	1.00
比較例	1	—	—	—	—	0.20	—	—
	2	—	—	—	—	—	0.30	—
	3	—	—	—	—	0.20	—	1.00

[0133]

[Table 2]

		難燃性 UL-94	フレイミング 合計秒数(秒)	ドリップ回数 (回)	透 明 性 HAZE (%)
実施例	1	V-0	4	0	5.4
	2	V-0	3	0	3.1
	3	V-0	2	0	2.0
	4	V-0	6	0	4.9
	5	V-0	4	0	3.8
	6	V-0	1	0	2.3
	7	V-0	3	0	3.0
	8	V-0	3	0	4.2
	9	V-0	2	0	2.0
	10	V-0	2	0	2.2
比較例	1	V-1	70	0	6.5
	2	V-1	63	0	5.1
	3	V-1	85	0	5.3

[0134]

[Effect of the Invention] Without polycarbonate spoiling the transparency and physical properties which it originally has, the fire-resistant polycarbonate resin composition of this invention can prevent dropping at the time of combustion, and may discover high fire retardancy. Therefore, the fire-resistant polycarbonate resin composition of this invention is suitably used as materials, such as various kinds of mold goods, for example, electricity and electronic parts, OA equipment parts, a car and a machine part, and building materials.

[Translation done.]



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(54) **FLAME-RETARDANT POLYCARBONATE RESIN COMPOSITION**

(57) This invention is a flame resistant polycarbonate resin composition characterized by blending 0.01-2 weight parts of a silicone compound (B)) wherein a main chain has a branch structure and having an aromatic group in an organic substituent, 0.01-2 weight parts of an alkali metal salt of an aromatic sulfonic acid (C) represented by the following general formula 1 (hereafter, referred to as general formula 1), and 0.05-5 weight parts of a fiber-forming fluorine-containing polymer (D), relative to 100 parts of a polycarbonate resin (A): General formula 1: $A_m-R-(SO_3M)_n$ (wherein, R is a phenyl group, naphthyl group, or a phenyl group or naphthyl group substituted by A, where A is at least one type of substituent chosen from a group comprising a

halogen atom, alkyl group, aryl group, vinyl group, alkoxy group, amino group, methyl ester group and ethyl ester group, and M is an alkali metal. Also, when R is phenyl, m and n are respectively the integers 0-5 and 1-2 ($m+n \leq 6$), and when R is naphthyl, m and n are respectively the integers 0-7 and 1-2 ($m+n \leq 8$).

The polycarbonate resin composition of this invention possesses superior flame resistance without losing shock resistance and moldability, and as it does not contain halogen fire retardants manufactured from chlorine and bromine compounds, there is no concern about generation of gases containing halogen from the fire retardant during combustion.

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Description

Field of the Invention

[0001] This invention relates to a fire-resistant polycarbonate resin composite. More specifically, it is related to a fire-resistant polycarbonate resin composite having improved fire retarding properties not containing halogen, i.e., chlorine and bromine, or flame-retarding agents, without impairing mechanical properties such as excellent shock resistance, fluidity and appearance of molded components which are characteristic of polycarbonate resins.

Background of the Invention

[0002] Polycarbonate resins are widely used in many fields, such as the electrical, electronic and OA fields, as engineering plastics having excellent transparency, shock resistance, heat resisting properties and electrical properties.

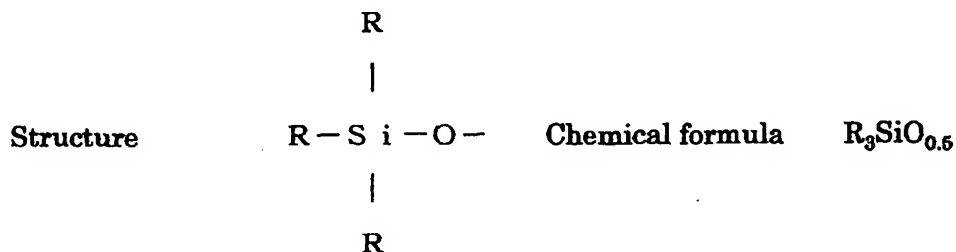
[0003] In the electrical, electronic and OA fields, many components are required to have superior fire retarding properties (UL94V) and advanced shock resistance, such as personal computer exterior parts. A polycarbonate resin is a highly fire-resistant plastic having self-extinguishing properties, but in order that it may satisfy safety requirements for electrical, electronic and OA equipment, still higher fire retarding properties equivalent to UL94V-0 or 94V-1 are needed.

[0004] Thus, to improve the fire retarding properties of a polycarbonate resin, a method has conventionally been used of blending it with a large amount of an oligomer or polymer of a carbonate derivative of brominated bisphenol A. However, although the fire retarding properties of a polycarbonate resin definitely improved when it was blended with a large amount of an oligomer or polymer of a carbonate derivative of brominated bisphenol A as a flame retarder, the shock resistance fell, and cracks easily developed in molded components.

[0005] Also, as it was mixed with a large amount of a halogen compound containing bromine, there was a concern that gas containing the halogen would be generated at the time of combustion, so a flame-retarding agent not containing chlorine or bromine was desired from the environmental viewpoint. Silicone compounds have high heat resistance, do not easily generate harmful gases during combustion and are also inherently safe, so many attempts have been made to use them as flame retarders.

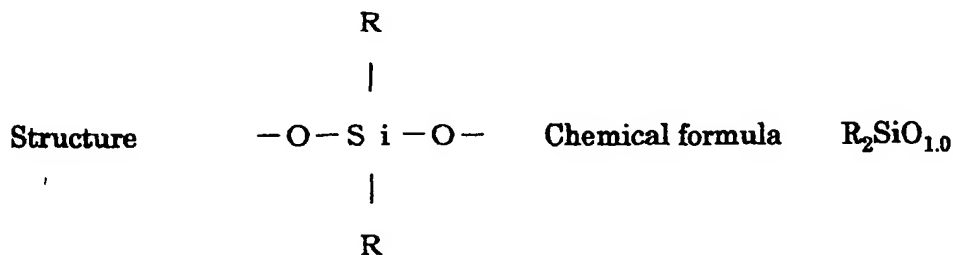
[0006] Silicone compounds which are flame retarders are polymers comprising at least the four siloxane units (M unit, D unit, T unit, Q unit) shown below.

(1) M unit



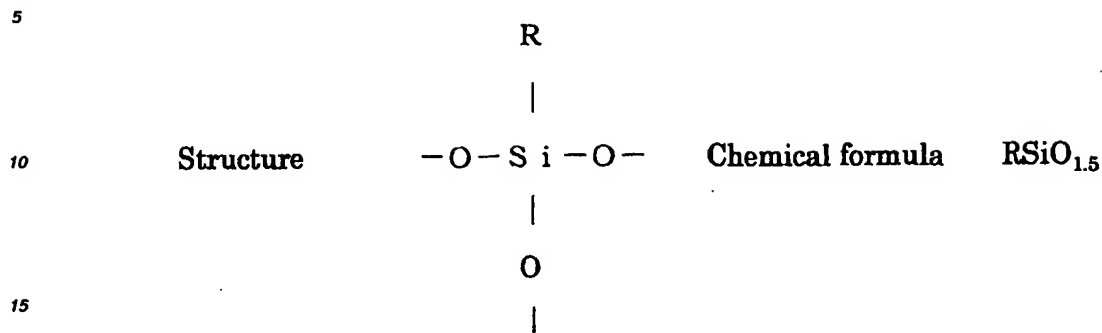
where, R is an organic substituent.

(2) D Unit



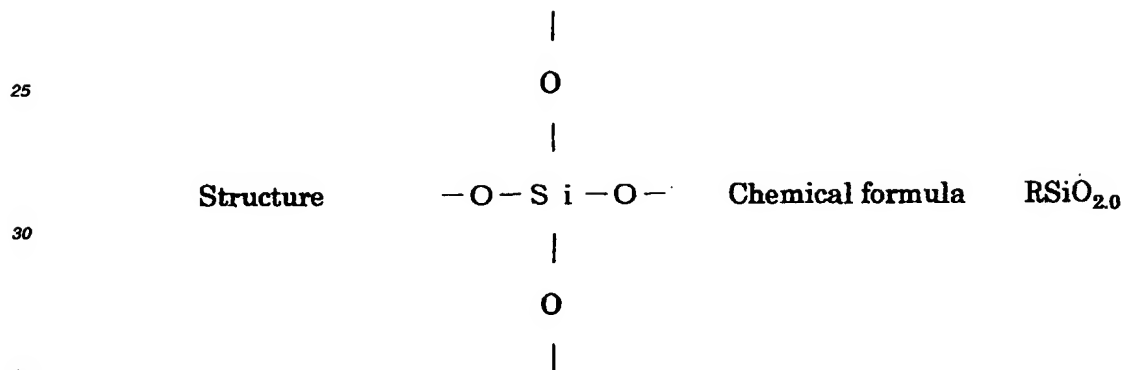
where, R is an organic substituent.

(3) T Unit



where, R is an organic substituent.

(4) Q Unit



[0007] Of these, the structure will be a branched structure if it contains a T unit and/or a Q unit.

[0008] Regarding the use of silicone compounds as flame retarders, silicone compounds with various organic substituents have been studied as disclosed in JP, 1-318069 (Kokai), and JP, 62-60421 (Kokoku).

[0009] However, there are very few compounds which conferred a significant flame-retarding effect when added alone, and as a large amount had to be added to satisfy the stringent requirements of electrical and electronic equipment, it had an adverse effect on the moldability and kneadability of the plastic or other necessary characteristics. Since it was disadvantageous also from the cost viewpoint, it was also impractical.

[0010] In an attempt to improve the flame-retarding effect of the silicone compound and reduce the addition amount, the use of a silicone compound in conjunction with a metal salt has also been reported. In this regard, the combined use of polydimethyl silicone, metal hydroxide and a zinc compound (JP, 2-150436 (Kokai)), polydimethyl silicone with a group IIa metal salt of an organic acid (JP, 56-100853 (Kokai)), a silicone resin, especially as represented by an M unit and a Q unit, with a silicone oil and a group IIa metal salt of an organic acid (JP, 3-48947 (Kokoku)), may be mentioned, but all are inferior in respect of fire retarding properties. There was a fundamental problem in that drastic curtailment of the addition amount was difficult.

[0011] The combined use of an organopolysiloxane having an epoxy group (gamma-glycidoxypopyl group), phenyl group and/or vinyl group together with an alkali metal salt and alkaline earth metal salt, etc. of an organic sulfonic acid (JP, 8-176425 (Kokai)) has also been reported. However, as this silicone compound contains highly reactive epoxy groups and vinyl groups, the silicone compounds react with each other at the elevated temperature during kneading with the polycarbonate resin, causing polymerization (gelation), so that it is difficult to knead it uniformly with the polycarbonate resin. Moreover, the overall viscosity also rises, so peeling, molding sink and unevenness in the moldability of the polycarbonate resin, and particularly the surface of the molded body, occur. Further, due to this gelation, the dispersibility of the silicone compound in the polycarbonate resin is inadequate, consequently it is difficult to achieve

a significant fire resistance, and there is also a problem in that strength properties, such as the impact strength of the molded product, also decrease.

Disclosure of the Invention

[0012] As a result of extensive research on the aforesaid problems, the Inventors discovered that a fire-resistant polycarbonate resin composite having superior fire retarding properties could be obtained without compromising shock resistance and moldability by using a specific silicone compound and an alkali metal salt of a specific aromatic sulfonic acid, with the further addition of a fiber-forming fluorine-containing polymer, as a flame retarder blended with the polycarbonate resin.

[0013] Moreover, since the fire-resistant polycarbonate resin composite of this invention does not contain halogen flame retarders, such as a bromine flame retarder, there is also no concern regarding the generation of gas containing halogen from the halogen flame retarder during combustion, and it also has excellent performance from the viewpoint of environmental protection.

[0014] Specifically, this invention relates to a fire-resistant polycarbonate resin composite comprising 0.01-8 weight parts of a silicone compound (B) having a branch structure in the main chain and an aromatic group in the organic substituents contained therein, and 0.01-2 weight parts of an alkali metal salt of an aromatic sulfonic acid represented by the following general formula 1, relative to 100 weight parts of a polycarbonate resin (A), and further containing a fiber-forming fluorine-containing polymer (D) in the composition.



(where R is phenyl, naphthyl, or phenyl or naphthyl substituted by A, where A is chosen from a halogen atom, alkyl group, aryl group, vinyl group, alkoxy group, amino group, methyl ester group and ethyl ester group, and M is an alkali metal. Moreover, when R is a phenyl group, m and n are respectively integers of 0-5 and 1-2, ($m+n \leq 6$) and when R is a naphthyl group, m and n are respectively 0-7 and 1-2 ($m+n \leq 8$).

[0015] Below, the fire-resistant polycarbonate resin composite of this invention will be described in detail.

[0016] The polycarbonate resin (A) used for this invention is a polymer obtained by the phosgene method wherein various dihydroxydiaryl compounds and phosgene are made to react, or the ester exchange method wherein a dihydroxydiaryl compound and a carbonic acid ester such as diphenyl carbonate, are made to react, a specific example being the polycarbonate resin manufactured from 2, 2-bis (4-hydroxy phenyl) propane (bisphenol A).

[0017] The above-mentioned dihydroxydiaryl compound, in addition to bisphenol A, may be a bis (hydroxyaryl) alkane such as bis(4-hydroxy phenyl)methane, 1, 1-bis(4-hydroxyphenyl)ethane, 2, 2-bis(4-hydroxy phenyl)butane, 2, 2-bis (4-hydroxyphenyl)octane, bis(4-hydroxyphenyl) phenylmethane, 2, 2-bis(4-hydroxyphenyl-3-methyl phenyl) propane, 1, 1-bis (4-hydroxy-3-t-butyl phenyl) propane, 2, 2-bis(4-hydroxy-3-bromophenyl)propane, 2, 2-bis(4-hydroxy-3, 5-dibromophenyl)propane or 2, 2-bis(4-hydroxy-3, 5-dichlorophenyl)propane, a bis(hydroxyaryl) cycloalkane such as 1, 1-bis(4-hydroxyphenyl)cyclopentane, 1, 1-bis (4-hydroxyphenyl)cyclohexane, a dihydroxydiaryl ether such as 4, 4'-dihydroxydiphenylether or 4, 4'-dihydroxy-3, 3'-dimethyldiphenyl ether, a dihydroxydiaryl sulfide such as 4, 4'-dihydroxydiphenylsulfide, a dihydroxydiaryl sulfoxide such as 4, 4'-dihydroxydiphenylsulfoxide or 4, 4'-dihydroxy-3, 3'-dimethyl diphenylsulfoxide, or a dihydroxydiaryl sulfone such as 4, 4'-dihydroxydiphenylsulfone or 4, 4'-dihydroxy-3, 3'-dimethyl diphenylsulfone.

[0018] These are used separately, or two or more may be used in combination. From the viewpoint of preventing discharge of gases containing halogen into the environment during combustion, it is preferable to use a compound unsubstituted by halogen. In addition, mixtures of piperazine, dipiperidyl hydroquinone, resorcinol or 4, 4'-dihydroxydiphenyl etc., may also be used.

[0019] Further, the aforesaid dihydroxyaryl compound can also be used mixed with phenol compounds having a valency of three or more, as indicated below.

[0020] Examples of phenols having a valency of three or more are phloroglucine, 4, 6-dimethyl, 2, 4, 6-tri (4-hydroxyphenyl)-heptene, 2, 4, 6-dimethyl-2, 4, 6-tri(4-hydroxyphenyl)-heptane, 1, 3, 5-tri(4-hydroxy phenyl)-benzole, 1, 1, 1-tri(4-hydroxyphenyl)-ethane and 2, 2-bis-[4, 4'-(4, 4'-dihydroxydiphenyl)-cyclohexyl]-propane.

[0021] The viscosity average molecular weight of the polycarbonate resin (A) is usually 10000-100000, but preferably 15000-35000. When this polycarbonate resin is manufactured, a molecular weight modifier, catalyst, etc. can be used if needed.

[0022] As the silicone compound (B) used in this invention, a compound wherein the main chain has a branched structure and containing an aromatic group as an organic substituent, such as shown in the following general formula 2, may be used.

10



2.

3

3

4

4

1

5

(where R is phenyl, naphthyl, or phenyl or naphthyl substituted by A, where A is chosen from a halogen atom, alkyl

group, aryl group, vinyl group, alkoxy group, amino group, methyl ester group or ethyl ester group, and M is an alkali metal. Moreover, when R is a phenyl group, m and n are respectively integers of 0-5 and 1-2, ($m+n \leq 6$) and when R is a naphthyl group, m and n are respectively 0-7 and 1-2 ($m+n \leq 8$).

[0030] As the alkali metal salt of the aromatic sulfonic acid which satisfies the general formula 1, for example, alkali metal salts such as p-toluenesulfonic acid, p-styrene sulfonic acid, 1-naphthalene sulfonic acid, isophthalic acid dimethyl-5-sulfonic acid, 2, 6-naphthalene disulfonic acid, benzenesulfonic acid, benzene disulfonic acid, 2, 4, 6-trichloro-5-sulfoisophthalic acid dimethyl, 2, 5-dichlorobenzene sulfonic acid, 2, 4, 5-trichlorobenzene sulfonic acid, p-iodobenzene sulfonic acid and 7-amino-1,3-naphthalene disulfonic acid, may be mentioned. These can be used separately, or more than one may be used in combination. Of these, one, two or more sodium salts and/or potassium salts chosen from 2, 4, 6-trichloro-5-sulfoisophthalic acid dimethyl, 2, 5-dichlorobenzene sulfonic acid, 2, 4, 5-trichlorobenzene sulfonic acid; or one, two or more salts chosen from p-toluenesulfonic acid, p-styrene sulfonic acid, 1-naphthalene sulfonic acid, isophthalic acid dimethyl-5-sulfonic acid, 2, 6-naphthalene disulfonic acid, benzenesulfonic acid and benzene disulfonic acid may conveniently be used.

[0031] Moreover, it is preferable that the sodium salt of p-toluenesulfonic acid, p-styrene sulfonic acid, 1-naphthalene sulfonic acid, isophthalic acid dimethyl-5-sulfonic acid, 2, 6-naphthalene disulfonic acid, benzenesulfonic acid and benzene disulfonic acid is adjusted so that the amount of sodium shown in the following Equation 1 is 0.001-0.05 weight parts relative to 100 weight parts of the polycarbonate (resin A).

Equation 1 :

Amount of sodium (weight parts) = blending amount (weight parts) of
sodium salt of aromatic sulfonic acid per 100 weight parts of polycarbonate (resin

A) x sodium molar fraction in the following Equation 2.

Equation 2 :

Sodium molar fraction = atomic weight of sodium/ molecular weight of
sodium salt of aromatic sulfonic acid

[0032] In the calculation of the sodium molar fraction shown in Equation 2, the atomic weight of each element is computed based on the atomic weight table (1995) of The International Union of Pure and Applied Chemistry (IUPAC). For example, for hydrogen it is 1.0080, and for carbon, oxygen, nitrogen, sulfur and sodium, it is 12.0107, 15.9994, 14.0067, 32.0666 and 22.9898, respectively. When the sodium amount is less than 0.001 weight parts, the proportion of sodium contained in the polycarbonate resin (A) is too low, so flame-retarding properties may decrease. On the other hand, when the sodium amount exceeds 0.05 weight parts, flame-retarding properties may again decrease. The preferred range is 0.002-0.04 weight parts.

[0033] The blending amount of the alkali metal salt (C) of the aromatic sulfonic acid shown in the general formula 1 is 0.01-2 weight parts to 100 weight parts of the polycarbonate resin (A). If it is less than 0.01 weight parts, fire retarding properties decrease, and if it is more than 2 weight parts, thermal stability decreases during extrusion molding which is undesirable. The preferred range is 0.01-1 weight parts, but more preferably 0.02-0.4 weight parts.

[0034] The fire-resistant polycarbonate resin composite of this invention may be mixed with other well-known flame retarders, for example halogen flame retarders, other silicone flame retarders or phosphorus flame retarders, etc. if needed. Examples of halogen flame retarders are brominated bisphenol A and polybromo-substituted aromatics homolog, examples of other silicone flame retarders are polyorganosiloxanes and polycarbonate-polyorganosiloxane copolymers, and examples of phosphorus flame retarders are phosphoric acid esters.

[0035] The fiber-forming fluorine-containing polymer (D) used by this invention may form a fiber structure (fibril-like structure) in the polycarbonate resin (A), examples being polytetrafluoroethylene, tetrafluoroethylene copolymers (for example, tetrafluoroethylene/hexa fluoropropylene copolymers), partially fluorinated polymers as shown in U.S. Pat. No. 4379910, and polycarbonates manufactured from fluorinated diphenols. When these are used together with a combination of the silicone compound (B) of this invention and the aromatic sulfonic acid alkali metal salt (C), in addition to preventing the dripping of the prior art, there is also a specific effect in preventing reduction of combustion time. The blending amount of the fiber-forming fluorine-containing polymer (D) is 0.05-5 weight parts to 100 weight parts of the polycarbonate resin (A). If the blending amount is less than 0.05 weight parts, there is less dripping prevention effect,

and if it is more than 5 weight parts, granulation becomes difficult which interferes with stable production.

[0036] The preferred range is 0.05-1 weight parts, but more preferably 0.1-0.5 weight parts. In this range, the balance of fire retarding properties, moldability and impact strength is even better.

[0037] Additives, such as various kinds of thermostabilizers, antioxidants, colorants, optical whitening agents, fillers, release agents, softeners, and antistatic agents, impact improving materials and other polymers may be blended with the polycarbonate resin (A) to the extent that they do not impair the effectiveness of this invention.

[0038] Examples of thermostabilizers are metal bisulfates such as sodium hydrogen sulfate, potassium hydrogen sulfate and lithium hydrogen sulfate, and metal sulfates such as aluminium sulfate. These are usually used in the range of 0-0.5 weight parts to 100 weight parts of the polycarbonate resin (A). Examples of fillers are glass fiber, glass beads, glass flakes, carbon fiber, talc powder, clay powder, mica, potassium titanate whisker, wollastonite powder and silica powder.

[0039] Examples of impact-improving materials are acrylic elastomers, polyester elastomers, core shell methyl methacrylate/butadiene/styrene copolymer, methyl methacrylate/acrylonitrile/styrene copolymer, ethylene/propylene rubber and ethylene/propylene/diene rubber.

[0040] Examples of other polymers are polyesters such as for example polyethylene terephthalate and polybutylene terephthalate; styrene polymers such as polystyrene, high impact polystyrene, acrylonitrile styrene copolymer and acrylic rubber-modified compounds of same, acrylonitrile/butadiene/styrene copolymer, acrylonitrile/ethylene/propylene/diene/rubber (EPDM)/styrene copolymer; polypropylene, and polymers usually used in the alloy of polycarbonate resins.

[0041] There is no particular limitation on the method of blending the various components in the fire-resistant polycarbonate resin composite of this invention, examples being well-known mixers such as a tumbler or ribbon blender, or melt kneading by an extruder.

[0042] There is no particular limitation on the method of forming the fire-resistant polycarbonate resin composite of this invention, it being possible to use the well-known injection molding method or injection stamping method.

Description of the Examples

[0043] This invention will now be described by way of examples, but this invention is not limited to these examples. "Part" is based on weight parts.

Examples 1-68 and Comparative Examples 1-33

[0044] Composites were melt extruded at a cylinder temperature of 280 degree C using a twin bis extruder (Kobe steel KTX- 37) of diameter 37mm based on the blending amounts shown in Tables 3-17 relative to 100 parts of the polycarbonate resin part manufactured from bisphenol A, to obtain various pellets.

[0045] The details of the raw materials used were respectively as follows.

1. Polycarbonate Resin (A) :

[0046] Caliber 200-20 (viscosity average molecular weight 19000), Sumitomo Dow Co.

2. Silicone Compound (B) :

[0047] The silicone compound (B) was manufactured according to the ordinary manufacturing method. Specifically, a diorganodichlorosilane, monoorganotrichlorosilane and tetrachlorosilane, or partial hydrolysis condensates thereof, were dissolved in an organic solvent according to the molecular weight of the silicone compound and the proportion of M units, D units, T units and Q units comprising the silicone compound, and water was added to hydrolyze the mixture so as to form a partially condensed silicone compound. Triorganochlorosilane was then added and reacted to terminate the polymerization, and the solvent was separated by distillation or the like. The structural characteristics of 19 types of silicone compounds synthesized by the aforesaid method are shown in Table 1.

Table 1

Silicone	D/T/Q ratio in main chain (mol ratio)	percentage of phenyl group* in organic substituent (mol %)	terminal group and its percentage (mol ratio)	weight average molecular weight**
a	0.7/9.3/0	60	solely methyl	12,000
b	2/8/0	60	solely methyl	7,000
c	2/8/0	60	solely methyl	12,000
d	2/8/0	60	solely methyl	70,000
e	2/8/0	60	solely methyl	250,000
f	2/8/0	60	solely methyl	300,000
g	2/8/0	60	solely hydroxyl	250,000
h	5/5/0	40	methyl	80,000
i	6.5/3.5/0	50	solely methyl	50,000
j	6.5/1.5/2	50	solely methyl	50,000
k	6.5/3.5/0	50	methyl/methoxy= 1/1	50,000
l	7.5/2.5/0	50	solely methyl	50,000
m	9/1/0	50	solely methyl	50,000
n	10/0/0	50	solely methyl	50,000
o	2/8/0	90	solely phenyl	70,000
p	2/8/0	45	solely methyl	70,000
q	2/8/0	25	solely methyl	70,000
r	2/8/0	10	solely methyl	70,000
s	2/8/0	0	solely methyl	70,000

Notes:

*: Phenyl groups are first contained in T units in a silicone comprising T units, and any remaining are in D units. If a phenyl group is attached to a D unit, compounds where one is attached have priority, two being attached if there are any remaining. Excepting for terminal groups, all organic substituents are methyl.

** : the weight average molecular weight is given to two significant figures.

3. Alkali metal salt of aromatic sulfonic acid (C) :

[0048]

Table 2

symbol	alkali metal salt of aromatic sulfonic acid (C)
C-1	2,5-dichlorobenzene sodium sulfonate
C-2	2,4,5- trichlorobenzene sodium sulfonate
C-3	sodium salt of 2,4,6-trichloro-5-sulfo isophthalic acid dimethyl
C-4	p-toluenesulfonic acid sodium
C-5	1- naphthalenesulfonic acid sodium
C-6	p-sodium styrenesulfonate
C-7	isophthalic acid dimethyl-5-sodium sulfonate
C-8	sodium benzenesulfonate
C-9	1-naphthalenesulfonic acid sodium

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Table 2 (continued)

symbol	alkali metal salt of aromatic sulfonic acid (C)
C - 10	m- benzene sodium disulfonate

4. Fiber-forming fluorine-containing polymer (D) :

[0049] Polytetrafluoroethylene (polychlorofluoron FA-500, Daikin Industries (abbreviated hereafter as PTFE).

6. Carbonate/oligomer of tetrabromobisphenol A:

[0050] BC-52, Great Lakes Chemicals (abbreviated as Br oligomer)

[0051] After drying the various pellets obtained at 125 degrees C for 4 hours, a test piece for fire-resistance evaluation (125 x 13 x 1.6mm and 125 x 13 x 3.2mm) was formed at 280 degrees C and an injection pressure of 1600 kg/cm² in an injection molding machine (J100-E-C5, Japan Steel Co.).

[0052] This test piece was left in a constant temperature room at a temperature of 23 degrees C and 50% humidity for 48 hours, and a fire-resistance evaluation was performed based on the UL94 test (flammability test for plastics for equipment components) defined by Underwriters Laboratories. In UL94V, fire retarding properties are evaluated from the remaining flame time and drip characteristics after bringing the flame of a burner in contact with a specimen of predetermined size held perpendicularly for 10 seconds, and is divided into the following classes.

	V-0	V-1	V-2
Remaining flame time for each sample	10 seconds or less	30 seconds or less	30 seconds or less
Total remaining flame time of five samples	50 seconds or less	250 seconds or less	250 seconds or less
Ignition of cotton by drip	No	No	Yes

[0053] The remaining flame time shown above is the length of time for which the specimen continues to burn with a flame after removing it from the ignition source, and ignition of cotton by drip is determined by whether or not a standard piece of cotton approximately 300mm under the lower end of the test piece is ignited by the drip from the test piece. If any of the five samples did not satisfy even one of the above criteria, it was evaluated as NR (not rated) for not satisfying V-2. The results are shown in Tables 3-17.

[0054] Using the various pellets obtained, injection molding was similarly performed to manufacture a test piece (3.2x12.7x63.5mm) for impact strength evaluation. Using this test piece, the impact strength with a notch was measured according to ASTM D-256. Also, as to the appearance of the molded component, a test piece was visually inspected before impact strength measurement, and the surface was examined for surface peeling or molding sink.

[0055] The results are shown in Tables 3-17, respectively.

[0056] In Tables 3-17:

- Numerical values for silicone, metal salt and PTFE are addition amounts (parts) relative to 100 parts of polycarbonate resin.
- The sodium amount shows the number of parts calculated by the following equation 1.

Equation 1 :

sodium amount (parts) = blending amount of aromatic sulfonic acid per 100

parts of polycarbonate resin (A) x sodium molar fraction from the following

Equation 2

Equation 2 :

sodium molar fraction = atomic weight of sodium/ molecular weight of sodium salt of aromatic sulfonic acid

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- In the evaluation results for flame-retarding properties in the table, the values () show the total (seconds) for the remaining flame time (combustion time after ignition) of the five samples. The values [] in the table show the number (number of the five samples) for which a standard piece of cotton ignited due to drip.
- moldability was evaluated from peeling of the surface layer, or unevenness or surface sink of the molded test piece, as follows.

○ : did not occur.

Δ : occurred in one to two of the five samples.

× : occurred in three or more of the five samples.

Table 3

		Examples						
		1	2	3	4	5	6	7
silicone a		2	-	-	-	-	-	-
silicone b		-	2	-	-	-	-	-
silicone c		-	-	2	-	-	-	-
silicone d		-	-	-	4	4	4	4
metal salt C-1		0.1	0.1	0.1	0.02	0.1	1.0	1.5
PTFE		0.3	0.3	0.3	-	-	-	-
flame-retarding properties UL94	3.2mm	V-0	V-0	V-0	V-0	V-0	V-0	V-1
	thick	(27)	(25)	(21)	(45)	(27)	(30)	(62)
	1.6mm	V-0	V-0	V-0	V-1	V-0	V-0	V-1
	thick	(35)	(36)	(27)	(62)	(35)	(40)	(88)
moldability		○	Δ	○	○	○	○	Δ
notched impact strength (Kgcm/cm)		63	60	61	62	61	62	59

Table 4

		Examples						
		8	9	10	11	12	13	14
silicone d		4	1	1	1	-	-	-
silicone e		-	-	-	-	0.5	4	7
metal salt C-1		0.1	0.02	0.6	1.2	0.1	0.1	0.1
PTFE		0.2	0.2	0.2	0.2	-	-	-
flame-retarding properties UL94	3.2mm	V-0	V-0	V-0	V-0	V-0	V-0	V-0
	thick	(20)	(32)	(22)	(38)	(30)	(25)	(41)
	1.6mm	V-0	V-0	V-0	V-1	V-0	V-0	V-0
	thick	(24)	(45)	(30)	(55)	(37)	(33)	(49)
moldability		○	○	○	○	○	○	○
notched impact strength (Kgcm/cm)		62	63	64	60	63	60	61

Table 5

		Examples						
		15	16	17	18	19	20	21
silicone e		0.02	0.5	4	7	-	-	-
silicone f		-	-	-	-	4	-	-
silicone g		-	-	-	-	-	4	4
metal salt C-1		0.1	0.1	0.1	0.1	0.1	0.1	0.1
PTFE		0.3	0.3	0.3	0.3	0.3	-	0.3
flame-retarding properties UL94	3.2mm	V-1	V-0	V-0	V-0	V-0	V-0	V-0
	thick	(75)	(15)	(13)	(27)	(24)	(31)	(17)
	1.6mm	V-1	V-0	V-0	V-0	V-0	V-0	V-0
	thick	(98)	(20)	(16)	(40)	(33)	(45)	(27)
moldability		○	○	○	○	Δ	○	○
notched impact strength (Kgcm/cm)		55	61	62	62	62	63	64

Table 6

		Examples						
		22	23	24	25	26	27	28
silicone h		2	2	2	2	2	2	2
metal salt C-1		0.1	0.1	0.1	0.1	0.1	0.1	0.1
PTFE		-	0.06	0.1	0.3	0.5	1	4
flame-retarding properties UL94	3.2mm	V-0	V-0	V-0	V-1	V-0	V-0	V-0
	thick	(38)	(28)	(18)	(17)	(16)	(30)	(34)
	1.6mm	V-1	V-0	V-0	V-1	V-0	V-0	V-0
	thick	(54)	(39)	(28)	(28)	(27)	(38)	(49)
moldability		○	○	○	○	○	○	○
notched impact strength (Kgcm/cm)		63	60	61	60	61	62	60

Table 7

		Examples							
		29	30	31	32	33	34	35	36
silicone i		2	2	-	-	-	-	-	-
silicone j		-	-	2	-	-	-	-	-
silicone k		-	-	-	2	-	-	-	-
silicone l		-	-	-	-	2	2	-	-
silicone m		-	-	-	-	-	-	2	2
metal salt C-1		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
PTFE		-	0.3	0.3	0.3	-	0.3	-	0.3

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Table 7 (continued)

		Examples							
		29	30	31	32	33	34	35	36
flame-retarding properties UL94	3.2mm	V-0	V-0	V-0	V-0	V-0	V-0	V-1	V-1
	thick	(31)	(20)	(17)	(28)	(48)	(33)	(60)	(53)
	1.6mm	V-0	V-0	V-0	V-0	V-1	V-0	V-2	V-1
	thick	(49)	(30)	(26)	(41)	(73)	(49)	[1]	(83)
moldability		○	○	○	○	○	○	Δ	Δ
notched impact strength (Kgcm/cm)		62	62	63	62	60	60	57	58

Table 8

		Examples							
		37	38	39	40	41	42	43	44
silicone o		2	2	-	-	-	-	-	-
silicone p		-	-	2	2	-	-	-	-
silicone q		-	-	-	-	2	2	-	-
silicone r		-	-	-	-	-	-	2	2
metal salt C-1		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
PTFE		-	0.3	-	0.3	-	0.3	-	0.3
flame-retarding properties UL94	3.2mm	V-0	V-0	V-0	V-0	V-0	V-0	V-1	V-1
	thick	(30)	(20)	(30)	(14)	(45)	(31)	(60)	(56)
	1.6mm	V-0	V-0	V-0	V-0	V-1	V-0	V-2	V-1
	thick	(42)	(33)	(45)	(23)	(66)	(44)	[1]	(78)
moldability		○	○	○	○	○	○	Δ	Δ
notched impact strength (Kgcm/cm)		62	62	63	62	60	60	57	58

Table 9

		Examples					
		45	46	47	48	49	50
silicone d		1	1	1	-	-	-
silicone h		-	-	-	2	2	2
metal salt C-1		0.1	-	-	0.1	-	-
metal salt C-2		-	0.1	-	-	0.1	-
metal salt C-3		-	-	0.1	-	-	0.1
PTFE		0.3	0.3	0.3	0.2	0.2	0.2
flame-retarding properties UL94	3.2mm	V-0	V-0	V-0	V-0	V-0	V-0
	thick	(8)	(7)	(18)	(17)	(16)	(27)
	1.6mm	V-0	V-0	V-0	V-0	V-0	V-0
	thick	(10)	(10)	(26)	(20)	(19)	(34)
moldability		○	○	○	○	○	○

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Table 9 (continued)

	Examples					
	45	46	47	48	49	50
notched impact strength (Kgcm/cm)	64	64	63	63	63	64

Table 10

	Examples					
	51	52	53	54	55	56
silicone d	1	1	1	1	1	1
metal salt C-4	0.05	0.05	0.01	0.01	0.4	0.4
amount of Na	0.0059	0.0059	0.00118	0.00118	0.0472	0.0472
PTFE	0.3	-	0.3	-	0.3	-
flame-retarding properties UL94	3.2mm thick	V-0 (10)	V-0 (18)	V-0 (26)	V-0 (42)	V-0 (25) (40)
	1.6mm thick	V-0 (12)	V-0 (24)	V-0 (35)	V-1 (58)	V-0 (33) (55)
moldability	○	○	○	○	○	○
notched impact strength (Kgcm/cm)	64	60	65	62	61	60

Table 11

	Examples					
	57	58	59	60	61	62
silicone d	1	1	1	1	1	1
metal salt C-5	0.05	0.05	-	-	-	-
metal salt C-6	-	-	0.05	0.05	-	-
metal salt C-7	-	-	-	-	0.05	0.05
amount of Na	0.005	0.005	0.0056	0.0056	0.0039	0.0039
PTFE	0.3	-	0.3 3	-	0.3 3	-
flame-retarding properties UL94	3.2mm thick	V-0 (12)	V-0 (21)	V-0 (10)	V-0 (19)	V-0 (18) (30)
	1.6mm thick	V-0 (16)	V-0 (29)	V-0 (14)	V-0 (27)	V-0 (23) (40)
moldability	○	○	○	○	○	○
notched impact strength (Kgcm/cm)	63	61	63	61	61	62

Table 12

	Examples					
	63	64	65	66	67	68
silicone d	1	1	1	1	1	1

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Table 12 (continued)

		Examples					
		63	64	65	66	67	68
5	metal salt C-8	0.05	0.05	-	-	-	-
	metal salt C-9	-	-	0.05	0.05	-	-
	metal salt C-10	-	-	-	-	0.05	0.05
10	amount of Na	0.0064	0.0064	0.0069	0.0069	0.00815	0.00815
	PTFE	0.3	-	0.3	-	0.3	-
15	flame-retarding properties UL94	3.2mm	V-0	V-0	V-0	V-0	V-0
		thick	(11)	(21)	(10)	(20)	(10)
		1.6mm	V-0	V-0	V-0	V-0	V-0
	thick	(16)	(28)	(16)	(27)	(15)	(26)
	moldability	○	○	○	○	○	○
20	notched impact strength (Kgc/cm)	63	64	64	63	63	63

Table 13

		Comparative examples				
		1	2	3	4	5
25	Br oligomer	-	-	-	-	5
	silicone	-	-	-	-	-
30	metal salt C-1	-	0.1	-	0.1	-
	PTFE	-	-	0.3	0.3	0.3
35	flame-retarding properties UL94	3.2mm	V-2	V-2	V-1	V-1
		thick	[5]	[5]	(162)	(150)
			(35)			
	1.6mm	V-2	V-2	V-2	V-2	V-1
	thick	[5]	[5]	[2]	[2]	(44)
	moldability	○	○	○	○	○
40	notched impact strength (Kgc/cm)	67	61	40	41	27

Table 14

		Comparative examples						
		6	7	8	9	10	11	12
45	silicone d	1	1	1	-	-	-	-
	silicone e	-	-	-	0.005	0.005	10	10
50	metal salt C-1	0.008	3	3	0.1	0.1	0.1	0.1
	PTFE	0.2	0.2	-	-	0.3	-	0.3
55	flame-retarding properties UL94	3.2mm	V-1	V-1	V-1	V-1	V-0	V-0
		thick	(84)	(98)	(125)	(131)	(106)	(44)
			(37)					
	1.6mm	V-1	V-1	V-1	V-2	V-2	V-1	V-0
	thick	(110)	(115)	(133)	[5]	[2]	(61)	(47)

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Table 14 (continued)

	Comparative examples						
	6	7	8	9	10	11	12
5 moldability	○	Δ	Δ	○	○	×	×
notched impact strength (Kgcm/cm)	65	43	48	63	40	61	62

Table 15

		Comparative examples					
		13	14	15	16	17	18
15 silicone h		2	-	-	-	-	-
silicone i		-	2	-	-	-	-
silicone k		-	-	2	-	-	-
silicone n		-	-	-	2	2	2
20 metal salt C-1		-	-	-	-	0.1	0.1
PTFE		-	-	-	-	-	0.3
25 flame-retarding properties UL94	3.2mm thick	V-1 (82)	V-1 (83)	V-1 (92)	V-2 [4]	V-1 (130)	V-1 (115)
	1.6mm thick	V-2 [2]	V-2 [2]	V-2 [3]	V-2 [5]	V-2 [5]	V-2 [3]
30 moldability		○	○	○	×	×	×
notched impact strength (Kgcm/cm)		63	62	62	46	45	45

Table 16

		Comparative examples							
		19	20	21	22	23	24	25	26
35 silicone o		2	-	-	-	-	-	-	-
silicone p		-	2	-	-	-	-	-	-
40 silicone q		-	-	2	-	-	-	-	-
silicone r		-	-	-	2	-	-	-	-
silicone s		-	-	-	-	2	2	2	2
45 metal salt C-1		-	-	-	-	-	0.1	0.1	0.3
PTFE		-	-	-	-	-	-	0.3	0.3
50 flame-retarding properties UL94	3.2mm thick	V-1 (97)	V-1 (80)	V-1 (89)	V-1 (121)	V-2 [4]	V-2 [4]	V-1 (136)	V-1 (122)
	1.6mm thick	V-2 [3]	V-2 [2]	V-2 [3]	V-2 [4]	V-2 [5]	V-2 [5]	V-2 [3]	V-2 [3]
55 moldability		○	○	Δ	Δ	×	×	×	×
notched impact strength (Kgcm/cm)		63	63	61	53	45	46	45	41

Table 17

	Comparative examples						
	27	28	29	30	31	32	33
silicone d	1	1	1	1	1	1	1
metal salt C-4	0.005	-	-	-	-	-	-
metal salt C-5	-	0.005	-	-	-	-	-
metal salt C-6	-	-	0.005	-	-	-	-
metal salt C-7	-	-	-	0.005	-	-	-
metal salt C-8	-	-	-	-	0.005	-	-
metal salt C-9	-	-	-	-	-	0.005	-
metal salt C-10	-	-	-	-	-	-	0.005
amount of Na (x0.001)	0.59	0.50	0.56	0.39	0.64	0.33	0.815
PTFE	0.2	0.2	0.2	0.2	0.2	0.2	0.2
flame-retarding properties UL94	3.2mm	V-1	V-1	V-1	V-1	V-1	V-1
	thick	(118)	(122)	(121)	(128)	(109)	(101)
	1.6mm	V-1	V-1	V-1	V-1	V-1	V-1
	thick	(132)	(140)	(135)	(150)	(133)	(130)
moldability	○	○	○	○	○	○	○
notched impact strength (Kgcm/cm)	64	64	64	65	63	65	64

[0057] As shown in Examples 1-68, the polycarbonate resin composition characterized in that 0.01-8 parts of a silicone compound having a main chain with a branch structure and aromatic groups (B) and 0.01-2 parts of an alkali metal salt (C) of the aromatic sulfonic acid shown by the general formula 1 are added, or a polycarbonate resin composition wherein 0.05-5 parts of a fiber-forming fluorine-containing polymer (D) are added to this combination, showed a very much larger flame-retarding effect than the polycarbonate resin alone without any additives (Comparative Example 1), the polycarbonate resin composition not containing both the silicone compound (B) and the alkali metal salt of an aromatic sulfonic acid (C) shown by the general formula 1 (Comparative Examples 2-4, 13-16, 19-23), or silicone compounds having a different structure to that of this invention (Comparative Examples 17-18, 23-26). Further, the reduction of impact strength of the polycarbonate resin composition which was a problem when conventional bromine flame-retarding agents were added as in Comparative Example 5, is remarkably improved as shown in this Example.

[0058] If the addition amount of the silicone compound (B) is less than 0.01 parts (Comparative Examples 9-10), flame resistance decreases as shown in Examples 12-18 and Comparative Examples 9-12, and if it is greater than 8 parts (Comparative Examples 11-12), moldability decreases.

[0059] If the addition amount of the aromatic sulfonic acid alkali metal salt (C) shown in the general formula 1 is less than 0.01 parts as shown in Examples 4-11 and Comparative Examples 6-8, flame resistance decreases (Comparative Example 6), and if it is larger than 2 parts, moldability and impact hardness decrease (Comparative Examples 7-8).

[0060] If, of the aromatic sulfonic acid alkali metal salts (C) shown by the general formula 1, the sodium content of the non-halogen sodium salts is adjusted to 0.001-0.05 parts, as shown in Examples 51-68, they show superior flame-retarding properties.

[0061] When the fiber-forming fluorine-containing polymer (D) is used together with the silicone compound (B) and aromatic sulfonic acid alkali metal salt shown by the general formula 1 (C), the drip prevention effect of the polycarbonate resin composition during combustion improves, and there is also a large reduction of combustion time, as shown in Examples 22-28, Examples 29 and 30, 33 and 34, 35 and 36, 37 and 38, 39 and 40, 41 and 42, 43 and 44. The fiber-forming fluorine-containing polymer used together with a non-halogen aromatic sodium sulfonate wherein the sodium content has been adjusted, and the silicone compound (B), not only improves the drip prevention effect of the polycarbonate resin composition but also largely reduces the combustion time, as shown in Examples 51-56 and Examples 57-68. This fluorine-containing polymer (D) not only functions as a simple drip inhibitor. There is also a synergistic effect in improving the overall flame retardancy in a combined system of this silicone compound (B) and this metal salt (C), or this silicone compound (B) and a non-halogen aromatic sulfonic acid sodium salt wherein the sodium

content is adjusted. Also, when it was attempted to manufacture a composition wherein 6 parts of this fluorine-containing polymer (D) were added to the combination of Example 22, granulation became difficult, and an evaluation could not be made.

[0062] When a branch unit of the main chain, i.e., a unit of formula $\text{RSiO}_{1.5}$ (T unit) and/or a unit of formula $\text{SiO}_{2.0}$ (Q unit) are included as shown in Examples 29-36 and Comparative Examples 16-18 in the structure of this silicone compound, the flame resistance, moldability and impact strength of the resulting polycarbonate resin composition largely improve as compared with a silicone which does not contain them (Comparative Examples 16-18), and these characteristics are enhanced in substances which contain 20 mol% or more relative to all the siloxane units ($\text{R}_{3-0}\text{SiO}_{2-0.5}$) (Examples 29-34). Further, in silicone compounds which contain 30 mol% or more of these branch units (Examples 29, 30), flame resistance and impact properties further improve, as is clear from a comparison of Examples 29, 30 and Examples 33, 34. If the amount of these branch units exceeds 95 mol%, an obvious flame-retarding effect may not easily be achieved. Hence, it is preferable that there are at least 20 mol% of the branch units, i.e., the units of formula $\text{RSiO}_{1.5}$ (T unit) and/or units of formula $\text{SiO}_{2.0}$ (Q unit), relative to all the siloxane units ($\text{R}_{3-0}\text{SiO}_{2-0.5}$, and a range of 30 mol% to 95 mol% is particularly suitable for flame resistance, moldability and impact strength.

[0063] Further, substances including units of formula $\text{SiO}_{2.0}$ (Q unit) have the same or higher degree of flame resistance compared with substances comprising only a unit of formula $\text{RSiO}_{1.5}$ (T unit) as branch unit, as shown in Examples 30, 31.

[0064] In addition, when there are aromatic groups (phenyl groups) in the organic substituents of the silicone compound (B), as shown in Examples 37-42, Examples 43-44 and Comparative Examples 23-26, the flame resistance, moldability and impact strength of the resulting polycarbonate resin composition improve compared with substances which do not contain them (Comparative Example 23-26). When they account for 20 mol% or more (Examples 37-42), flame resistance, moldability and impact strength are further improved, and when they account for 40 mol% or more (Examples 37-40) as shown in Examples 37-40 and Examples 41-42, the flame-retarding effect is greatly enhanced. When the aromatic groups (phenyl groups) in the organic substituents account for more than 95%, an obvious flame-retarding effect may not easily be achieved. Hence, it is preferable that the aromatic groups (phenyl groups) in the organic substituents account for 20 mol % or more, with a range of 40 mol% to 95 mol% being particularly preferred from the viewpoint of flame-retarding properties, moldability and impact strength.

[0065] Regarding the terminal groups of silicone compound (B), substances containing methyl groups (Examples 13, 17, 30), phenyl groups (Examples 37-38), hydroxy groups (Examples 20-21) and alkoxy groups (methoxy groups) (Example 32) show good flame resistance, moldability and impact strength, as seen from Examples 13 and 17, 20-21, 30 and 32, 37-38. It is seen that methyl groups confer better flame resistance than hydroxy terminal groups, as shown in Examples 13 and 17, 20 and 21, and that methyl groups confer better flame resistance than alkoxy groups, as shown in Examples 30 and 32. Further, methyl groups confer better flame resistance than phenyl groups. In addition, in substances including epoxy groups (gamma glycidoxypopyl groups) and vinyl groups, reactivity is particularly high, so the silicone compounds react with each other when kneading with the polycarbonate resin, the silicone compound (B) gels, the moldability of the polycarbonate resin largely decreases and dispersibility of the silicone compound (B) in the polycarbonate resin decreases, so sufficient flame-retarding effect and impact strength cannot be obtained. Therefore, as the terminal group of the silicone compound (B), methyl is the most preferable.

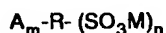
[0066] Regarding the molecular weight of this silicone compound (B), 5000-500000 is suitable and 10000-270000 is particularly suitable from the viewpoint of moldability and flame resistance, as understood from Example 2, 3, 17, 19. As the aromatic sulfonic acid alkali metal salt shown by the general formula 1 (C), as seen in Examples 45-50, 2,5-dichlorobenzene sodium sulfonate (C-1), 2,4,5-trichlorobenzene sodium sulfonate (C-2) or sodium salt of 2,4,6-trichloro-5-sulfo isophthalic acid dimethyl (C-3) are suitable, where 2,5-dichlorobenzene sodium sulfonate and 2,4,5-trichlorobenzene sodium sulfonate are particularly preferred. On the other hand, as the non-halogen aromatic sodium sulfonate, as shown in Examples 51-68, p-toluenesulfonic acid sodium (C-4), 1-naphthalenesulfonic acid sodium (C-5), p-sodium styrenesulfonate (C-6), isophthalic acid dimethyl-5-sodium sulfonate (C-7), sodium benzenesulfonate (C-8), 1-naphthalenesulfonic acid sodium (C-9) and m-benzene sodium disulfonate (C-10) are suitable, where p-toluenesulfonic acid sodium and 1-naphthalenesulfonic acid sodium are particularly preferred.

[0067] From the above results, it is seen that when 0.1-8 parts of the silicone compound (B) and 0.01-2 parts of the aromatic sulfonic acid alkali metal salt (C) shown in the general formula 1 of this invention are used together, a very large flame-retarding effect on the polycarbonate resin (A) is obtained that cannot be achieved if the silicone compound (B) is used alone. Further, regarding the non-halogen aromatic sodium sulfonate, a highly superior flame resistance effect is achieved by adjusting the sodium content to the range of 0.001-0.05 parts. This is a special synergistic effect found only in a combination of these components. Further, when 0.05-5 parts of the fiber-forming fluorine-containing polymer (D) is used in combination with the above components, not only does the drip prevention effect on the polycarbonate resin during combustion improve, but there is also a large effect in reduction of combustion time, and there is a synergistic effect in improving the overall flame retardance only in the combined system of this silicone compound (B) and this metal salt (C).

[0068] The polycarbonate resin composition of this invention possesses superior flame resistance without losing shock resistance and moldability, and as it does not contain halogen fire retardants manufactured from chlorine and bromine compounds, there is no concern about generation of gases containing halogen from the fire retardant during combustion.

Claims

1. A polycarbonate resin composition comprising, relative to 100 weight parts of a polycarbonate resin (A), 0.01-8 weight parts of a silicone compound (B) wherein a main chain has a branch structure and having an aromatic group in an organic substituent and 0.01-2 weight parts of an alkali metal salt of an aromatic sulfonic acid (C) represented by the following general formula:



(wherein, R is a phenyl group, naphthyl group, or a phenyl group or naphthyl group substituted by A, where A is at least one type of substituent chosen from a group comprising a halogen atom, alkyl group, aryl group, vinyl group, alkoxy group, amino group, methyl ester group and ethyl ester group, and M is an alkali metal. Also, when R is phenyl, m and n are respectively the integers 0-5 and 1-2 ($m+n \leq 6$), and when R is naphthyl, m and n are respectively the integers 0-7 and 1-2 ($m+n \leq 8$).

2. The flame resistant polycarbonate resin composition as defined in Claim 1, further comprising 0.05-5 weight parts of a fiber-forming fluorine-containing polymer (D).
3. The flame resistant polycarbonate resin composition as defined in Claim 1, wherein the blending amount of the silicone compound (B) is 0.1-5 weight parts, and the blending amount of the alkali metal salt (C) is 0.01-1 weight parts.
4. The flame resistant polycarbonate resin composition as defined in Claim 2, wherein the blending amount of said silicone compound (B) is 0.1-5 weight parts, the blending amount of said alkali metal salt (C) is 0.01-1 weight parts, and the blending amount of said fluorine-containing polymer (D) is 0.05-1 weight parts.
5. The flame resistant polycarbonate resin composition as defined in any of Claims 1-4, wherein the above silicone compound (B) contains a unit of formula $RSiO_{1.5}$ (T unit) and/or a unit of formula $SiO_{2.0}$ (Q unit) which accounts for at least 20 mol% of the total siloxane units ($R_{3-0}SiO_{2-0.5}$).
6. The flame resistant polycarbonate resin composition as defined in any of Claims 1-5, wherein aromatic groups account for at least 20 mol% of the organic substituents contained in said silicone compound (B).
7. The flame resistance polycarbonate resin composition as defined in any of Claims 1-6, wherein said aromatic group is a phenyl group, the terminal group in said organic substituent is chosen from a group comprising methyl, phenyl, hydroxy and alkoxy, and the remaining organic substituents are methyl.
8. The flame resistant polycarbonate resin composition as defined in any of Claims 1-4, wherein said alkali metal salt (C) is an alkali metal salt of at least one kind of aromatic sulfonic acid chosen from a group comprising p-toluenesulfonic acid, p-styrenesulfonic acid, 1-naphthalenesulfonic acid, isophthalic acid dimethyl-5-sulfonic acid, 2,6-naphthalenedisulfonic acid, benzenesulfonic acid, benzene disulfonic acid, 2,4,6-trichloro-5-sulfo-isophthalic acid dimethyl, 2,5-dichlorobenzene sulfonic acid and 2,4,5-trichlorobenzene sulfonic acid.
9. The flame resistant polycarbonate resin composition as defined in Claim 8, wherein said alkali metal salt (C) is the sodium salt and/or potassium salt of at least one type of aromatic sulfonic acid chosen from a group comprising 2,4,6-trichloro-5-sulfo-isophthalic acid dimethyl, 2,5-dichlorobenzene sulfonic acid and 2,4,5-trichlorobenzene sulfonic acid.
10. The flame resistant polycarbonate resin composition as defined in Claim 8, wherein said alkali metal salt (C) is the sodium salt of at least one type of aromatic sulfonic acid chosen from a group comprising p-toluenesulfonic acid, p-styrenesulfonic acid, 1-naphthalenesulfonic acid, isophthalic acid dimethyl-5-sulfonic acid, 2,6-naphtha-

lene disulfonic acid, benzene sulfonic acid and benzene disulfonic acid.

11. The flame resistant polycarbonate resin composition as defined in Claim 10, wherein the sodium content of said sodium salt is 0.001-0.05 weight parts per 100 weight parts of the polycarbonate resin (A).

12. The flame resistance polycarbonate resin composition as defined in Claim 11, wherein the sodium content of said sodium salt is 0.002-0.04 weight parts per 100 weight parts of the polycarbonate resin (A).

13. The flame resistant polycarbonate resin composition as defined in Claim 2 or 4, wherein said fluorine-containing polymer (D) is polytetrafluoroethylene.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP00/02472

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C08L69/00, C08K5/42// (C08L69:00, C08L27:12, C08L83:04)		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C08L69/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-2000 Toroku Jitsuyo Shinan Koho 1994-2000 Kokai Jitsuyo Shinan Koho 1971-2000 Jitsuyo Shinan Toroku Koho 1996-2000		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, 4387176, A (General Electric Company), 07 June, 1983 (07.06.83), Column 21, lines 17 to 49 & JP, 59-500099, A page 1, lower left column, line 2 to page 1, lower left line 5)	1-13
Y	JP, 9-151309, A (Daicel Chemical Industries, Ltd.), 10 June, 1997 (10.06.97), page 2, left column, lines 2 to 29 (Family: none)	1-13
Y	JP, 11-92678, A (Asahi Chemical Industry Co., Ltd.), 06 April, 1999 (06.04.99), page 2, left column, lines 2 to 13; page 2, left column, lines 27 to 830; page 2, left column, lines 37 to 43 (Family: none)	2, 4, 13
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search 10 July, 2000 (10.07.00)		Date of mailing of the international search report 18 July, 2000 (18.07.00)
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